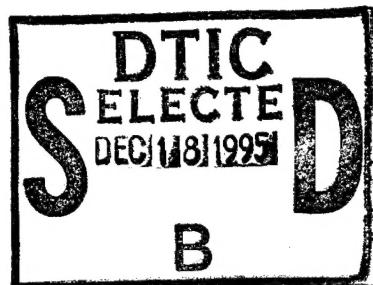


SILICONE MODIFIED RESINS FOR GRAPHITE FIBER LAMINATES

L. W. Frost and G. M. Bower

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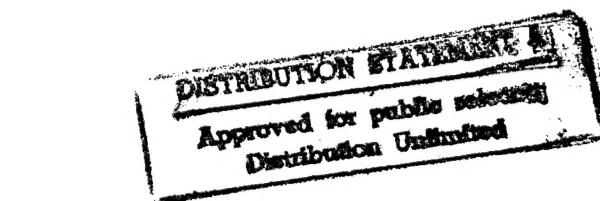
September 28, 1979

WESTINGHOUSE R&D FINAL REPORT 79-9B7-SICOP-R1

Prepared for
NASA/Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135

Contract NAS3-21373

19951214 131



DEPARTMENT OF DEFENSE
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-- 1 - AD NUMBER: D431645
-- 5 - CORPORATE AUTHOR: WESTINGHOUSE RESEARCH AND DEVELOPMENT CENTER
-- PITTSBURGH PA
-- 6 - UNCLASSIFIED TITLE: SILICONE MODIFIED RESINS FOR GRAPHITE FIBER
-- LAMINATES,
--10 - PERSONAL AUTHORS: FROST,L. W. ; BOWER,G. M. ;
--11 - REPORT DATE: SEP 28, 1979
--12 - PAGINATION: 77P
--14 - REPORT NUMBER: 79-987-SICOP-R1
--15 - CONTRACT NUMBER: NAS3-21373
--18 - MONITOR ACRONYM: NASA
--19 - MONITOR SERIES: CR-159750
--20 - REPORT CLASSIFICATION: UNCLASSIFIED
--22 - LIMITATIONS (ALPHA): APPROVED FOR PUBLIC RELEASE; DISTRIBUTION
-- UNLIMITED. ~~AVAILABILITY: NATIONAL TECHNICAL INFORMATION SERVICE~~
-- ~~SPRINGFIELD, VA 20161. NASA CR 159750.~~
--33 - LIMITATION CODES: 1 [REDACTED]

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SILICONE MODIFIED RESINS FOR GRAPHITE FIBER LAMINATES

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SUMMARY

When graphite fiber composites are burned, the liberated fibers may settle on electrical apparatus and cause severe damage. This problem can be minimized by bonding the fibers with silicone modified laminating resins that leave a siliceous residual char when they are burned.

During the first year of this program, 85 silicone modified resins have been synthesized and evaluated for this application. Included were unsaturated polyesters, thermosetting methacrylates, epoxies, polyimides, and phenolics. Neat resins were judged in terms of Si content, homogeneity, hardness, char formation, and thermal stability. Char formation was estimated by thermogravimetry to 1,000°C in air and in N₂. Thermal stability was evaluated by isothermal weight loss measurements for 200 hrs in air at three temperatures.

Four silicone modified epoxies were selected for evaluation in unidirectional filament wound graphite laminates. Neat samples of these resins had 1,000°C char residues of 25-50%. The highest flexural values measured for the laminates were a strength of 140 kpsi and a modulus of

10 Mpsi. The highest interlaminar shear strength was 5.3 kpsi. Two of the resins were used to make 8" x 8" x 0.1" flat unidirectional laminates, which have been shipped to NASA-Lewis for further evaluation.

INTRODUCTION

Composites made from graphite fibers bonded with epoxy or other resins are among the strongest and stiffest materials available. They have found use in applications ranging from golf clubs to airplane wings. However, an unexpected problem has arisen. When such composites are involved in a fire that is sufficiently intense to burn off the resin, graphite fibers are released into the air. The fibers are electrical conductors, and if they settle on electrical equipment, severe damage can be done.

One method of minimizing the hazard is to use laminating resins that leave a non-volatile residue (char) when they burn. The residue may be expected to trap the graphite fibers and prevent their dispersal. The purpose of the research described in this report is to prepare silicone modified polymers that leave a siliceous residue when they burn and to evaluate their usefulness as laminating resins for graphite fibers. Silicone modified versions of the following types of polymers have been studied: unsaturated polyesters, thermosetting methacrylates, epoxies, phenolics, and polyimides.

Polymers in each class have been prepared and evaluated for curing characteristics, hardness, and char formation at 1,000°C.

In addition, weight losses of selected resins have been measured at 175, 200, and 225°C for 200 hrs. Graphite fiber laminates have been made from the more promising resins. Physical properties and aging characteristics were determined. Laminate specimens 8" x 8" x 0.1" from two of the resins were submitted to the Lewis Research Center, NASA, for further evaluation.

The following sections describe work done on this project from July 1, 1978 to August 31, 1979.

SYMBOLS

A considerable number of complex polymers have been prepared in the course of the project. Nomenclature for such materials becomes very cumbersome unless a system of shorthand symbols is used. The system used in this report is designed to identify each polymer quickly and concisely and to identify a particular batch of material. A separate system has been devised for each purpose.

Each polymer is assigned an identification number which indicates the general class of material and identifies a particular composition within the class. The following letter designations are used for the various classes:

ES	ester silicone
EpS	epoxy silicone
EpIS	epoxy imide silicone
PS	phenolic silicone
IS	imide silicone
MaS	methacrylate silicone.

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A number is used with each letter designation. Numbers were assigned consecutively to compositions as they were made for the first time. If a given composition was prepared again it was not assigned a new number unless there was a substantial difference in the method of preparation.

Each batch or specimen is assigned a batch number consisting of three parts: notebook number, page number, and item on the page. Thus, for example, D98-96-2 refers to the second item on page 96 of notebook D98. This number provides a quick reference to the original records and also distinguishes among different batches of the same polymer composition or between different specimens of cured resin, laminates, etc.

Abbreviations are also used for many of the chemical compounds which are referred to repeatedly. In addition to standard symbols for the elements, the following symbols are used for particular chemical groups or compounds:

APS	3-aminopropyltriethoxysilane
BPA	2,2-bis(4-hydroxyphenyl)propane
BTDA	3,4,3',4'-benzophenonetetracarboxylic dianhydride
DMCS	dimethyldichlorosilane
DME	1,2-dimethoxyethane
DMES	dimethyldiethoxysilane
DMF	N,N-dimethylformamide
DMPS	dimethylphenylchlorosilane
EEA	2-ethoxyethyl acetate
EG	ethylene glycol
E8	Epon 828 (diglycidyl ether of BPA)
FU	fumaric acid
GL	glycerol
GPS	3-glycidoxypolytrimethoxysilane

HMDS	hexamethyldisilazane
HXA	hexamethylenetetramine
IP	isophthalic acid
MA	maleic anhydride
MAPS	3-methacryloxypropyltrimethoxysilane
MOE	2-methoxyethanol
MPCS	methylphenyldichlorosilane
MPMS	methylphenyldimethoxysilane
NBA	5-norbornene-2,3-dicarboxylic anhydride
PMDA	pyromellitic dianhydride
PO	propylene oxide
ST	styrene
TBP	tert-butyl perbenzoate
THF	tetrahydrofuran
TMA	trimellitic anhydride
TMCS	trimethylchlorosilane
TMES	trimethylethoxysilane
VCS	vinyltrichlorosilane

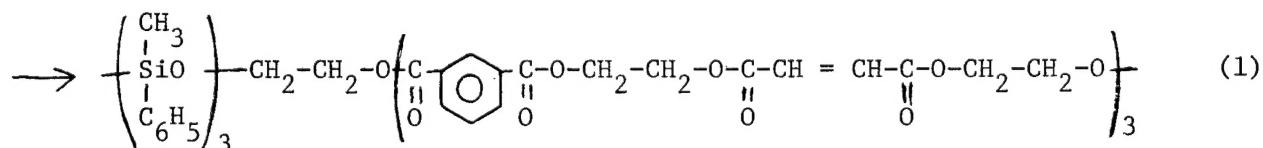
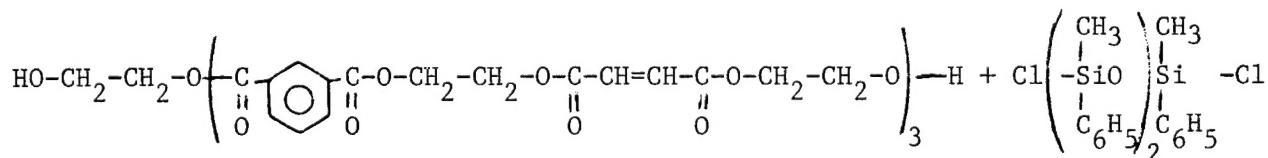
POLYMER PREPARATION

Silicone Modified Polyesters

Synthetic plan. - The first step in the synthesis of silicone modified polyesters was the preparation of a hydroxy terminated unsaturated polyester of moderate molecular weight. Most of these polymers were prepared from ethylene glycol (EG), isophthalic acid (IP), and fumaric acid (FU), using an excess of EG to assure hydroxy termination and low acid number. In some cases, part of the EG was replaced by glycerol (GL) to give a polymer containing hydroxy groups along the chain as well as at the ends. Very low molecular weight hydroxy terminated esters were made from dibasic acids and propylene oxide (PO).

The second step in the synthesis was the preparation of a polysiloxane having reactive groups, such as chloro or alkoxy, attached to the terminal silicon atoms. In most cases these materials were difunctional linear polymers composed of dimethyl or methylphenyl siloxane groups. Some siloxanes were also made in which either an endblocking group, such as trimethylsiloxy, or a monosubstituted group, such as vinylsilsesquioxy, or both were included in the structure. Some of these siloxanes had functionalities greater or less than two.

The third step was the reaction of a polyester from the first step and a polysiloxane from the second step, with the elimination of either HCl or an alcohol. The product was a block copolymer containing polysiloxane and unsaturated polyester segments. In some cases a dichloro or dialkoxy silane was used instead of a polysiloxane to give a polymer in which each of the silicon containing blocks incorporated only one silicon atom. The following idealized equation exemplifies the third step:



The product of the third step was mixed with an unsaturated compound such as styrene (ST), together with an initiator such as

tert-butyl perbenzoate (TBP). When the mixture was heated, copolymerization occurred between the unsaturated compound and the double bonds in the polyester to give a crosslinked structure.

Preparation of polyester intermediates. - Table 1 summarizes the compositions of the various polyester intermediates used in the preparation of silicone modified polyester resins. With the exception of batches F61-151-1 and F62-12-1 they were made by a heat-and-sparge procedure at temperatures of 200-240°C. In this method some EG is lost with the byproduct water. To compensate for the loss, additional EG was added during the cook. It was assumed that no volatilization of the other reactants occurred. All batches were reacted to an acid number of less than 5, so essentially all terminal groups can be assumed to be hydroxyl.

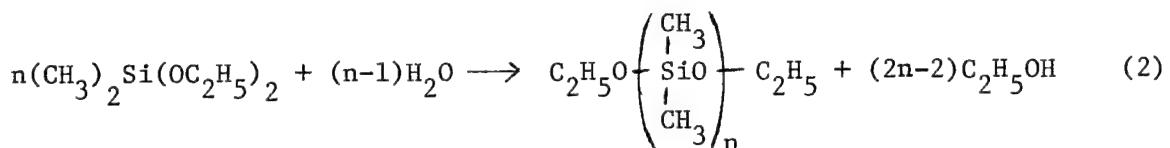
Hydroxyl content was determined directly by the method of Siggia¹. This value, together with the initial quantities of nonvolatile reactants, was used to determine the reactant ratios shown in Table 1. Molecular and equivalent weights were obtained from the same data, assuming two hydroxyl groups per polymer molecule for the polymers prepared from difunctional reactants. This assumption cannot be made for the polymers containing GL, and molecular weights are not reported for these materials.

Other things being equal, reducing the molecular weight of the polyester segments increases the silicone content of a silicone modified polyester resin. Low molecular weight polyester batches F61-151-1 and F62-12-1 were made for this purpose from PO and FU, using a modification of the method of Wygant, et al.².

TABLE 1 - COMPOSITIONS OF POLYESTER INTERMEDIATES

Batch No.	Composition, Moles					% OH	MW	Equivalent Wt.	
	IP	FU	EG	GL	PO			OH	Double Bond
F61-94-1	1	1	2.54	0	0	5.0	680	340	370
F61-94-2	1	1	2.95	0	0	8.2	415	210	390
F61-94-3	1	1	2.49	0	0	4.6	740	370	360
F61-96-1	1	1	2.33	0	0	3.2	1,060	530	350
F61-99-1	0	1	1.32	0	0	6.7	510	255	160
F61-126-1	1	1.4	3.43	0	0	7.7	440	220	325
F61-131-1	1	1.4	2.80	0	0	3.3	1,030	515	300
F61-138-1	1	1	0.97	1.36	0	8.7	--	200	400
F61-139-1	1	1	1.54	0.78	0	6.4	--	270	380
F61-149-1	0	1	1.13	0	0	3.0	1,130	565	150
F61-150-1	0	1	1.64	0	0	12.0	280	140	180
F61-151-1	0	1	0	0	1.67	11.0	310	155	207
F61-155-1	0	1	1.37	0	0	7.6	450	220	165
F62-12-1	0	1	0	0	1.5	8.8	390	190	190
F62-25-3	1	1	0.81	1.36	0	7.5	--	230	390
F62-34-1	1	1.4	2.98	0	0	4.65	730	370	305
F62-39-1	1	1.4	3.03	0	0	5.0	680	340	310

Preparation of polysiloxane intermediates. - Partial hydrolysis
of a difunctional organosilicon monomer gives a mixture of linear
siloxanes of various molecular weights, having reactive endgroups. A
preparation of this type is the reaction of dimethyldiethoxysilane (DMES)
with water:



Fletcher and Hunter³ have reported the preparation of a series of siloxanes by this method, using NaOH as a catalyst. Their procedure was repeated several times, but yields were low. Two factors were identified which contributed to the low yields. One was the use of a basic catalyst in the hydrolysis, as recommended by Fletcher and Hunter. This procedure was found to give mostly a mixture of high polymer and unreacted monomer, whereas an acidic catalyst gave a better yield of the desired intermediate products. The second factor was the existence of an azeotrope (bp 77°C), consisting of 83% ethanol and 17% dimethyldiethoxysilane.⁴ When ethanol was distilled from the reaction mixture, a substantial amount of unreacted monomer co-distilled and was inadvertently discarded. When HCl was used as a catalyst, with a H₂O/DMES mole ratio of 0.75, very little unreacted monomer was left. The yield of ethoxy terminated distilled oligomers containing 3-11 silicon atoms per molecule was 77%.

A potentially less expensive approach to the preparation of a similar product is the reaction of dimethyldichlorosilane (DMCS) with

ethanol and water. Several runs of this type were made. Best results were obtained by adding an excess of anhydrous ethanol to stirred DMES, boiling off as much HCl as possible (about 60% of total), adding triethyl-amine to neutralize the remaining HCl, and finally adding H_2O ($H_2O/DMCS$ mole ratio of 0.28). The yield of distilled oligomers containing 2-12 silicon atoms per molecule was 55%.

Products from several runs of both types were combined and distilled to give the fractions shown in Table 2. Estimations of average chain length were made from refractive index, density, elemental analysis, and NMR. The refractive index and density estimates were obtained by interpolation from the data of Fletcher and Hunter³. The various estimates agreed reasonably well, and the average values were used for stoichiometric calculations.

A similar series of siloxanes was prepared by partial hydrolysis of methylphenyldimethoxysilane (MPMS), using a modification of the method of Fletcher and Hunter. Because of their high boiling points, the products were not distilled, and average chain lengths were calculated from the ratio of water to monomer. Table 3 shows the intermediates made in this way.

Ethoxy terminated dimethylsiloxane oligomers of intermediate molecular weight have been reported to be more readily obtainable than the corresponding chlorosiloxanes.³ However, partial hydrolysis of chlorosilanes in a one phase system with a mutual solvent has been reported by Patnode and Wilcock⁵ and by Daudt and Hyde⁶ to give good yields of the desired products. A modification of their methods was used to hydrolyze DMCS and methylphenyldichlorosilane (MPCS) to chloro-terminated siloxanes,

TABLE 2 - ETHOXY TERMINATED DIMETHYLSILOXANE FRACTIONS

Fraction No.	D98-70-1	D98-70-4	D98-71-1	D98-74-6	D98-74-2	D98-74-5
bp, °C/mm Hg	38/0.5-45/0.15	101/0.2-103/0.2	>180/0.2	140-161/740	162-242/740	30-64/0.25
n_D^{20}	1.3923	1.3981	1.4024	1.3864	1.3911	1.3923
d_4^{20}			0.8574	0.9132	0.9241	0.9406
Analysis, %						
C		46.07	38.33	37.43	36.72	
H		10.24	9.12	8.74	9.02	
Si		17.98	29.12	28.97	31.29	
Relative Number of Protons by NMR						
CH ₃ -Si-	100	100	100	ca. 14	ca. 14	ca. 14
CH ₃ -C-	27.8	19.2	7.1	14.1	14.1	14.1
-O-CH ₂ -C-	17.6	9.1	3.7	18.0	18.0	18.0
Siloxane Units Per Chain From						
n_D^{20}	3.0	6.0	1.7	2.65	2.65	2.65
NMR (CH ₃ -C-)	3.6	5.2				
NMR (O-CH ₂ -C-)	3.8	7.3				
d_4^{20}			1.4	3.75	4.95	4.95
Analysis						
C		1.37	4.46	5.44	5.44	5.49
H		1.61	4.64	8.31	8.31	5.30
Si		0.90	3.32	3.25	3.25	4.75
Average	3.5	6.2	15.4	1.4	3.8	5.0
						6.3

TABLE 3 - METHOXY-TERMINATED METHYL PHENYL SILOXANES

Run No.	F61-28-3, F62-15-1	F61-28-4	F61-28-5	F62-14-1
Siloxane units, calc.	3	8	20	5
MPMS				
g	227.9	227.9	227.9	227.9
moles	1.25	1.25	1.25	1.25
Water				
g	15.01	19.71	21.39	18.1
moles	0.833	1.094	1.188	1.00
Final Product				
g	169.9	141.1	136.2	--
Yield, %	90	86	79	--
n_D^{20}	1.5242	1.5354	1.5443	1.5335
d_4^{20}	1.0837	1.1014	1.1178	--
visc., cstks, 25°C	18.2	106	490	--

which have been found to react more readily with alcohols than do the corresponding alkoxy derivatives. Tetrahydrofuran (THF) was used as a mutual solvent in the preparation of siloxane intermediates which were distilled to give the fractions shown in Table 4. The H_2O /monomer ratio was 0.5 for DMCS and 0.67 for MPCS.

TABLE 4 - CHLORO-TERMINATED SILOXANES

Fraction No.	Monomer	Bp, °C/mm	% Cl	Siloxane Units ^a	Yield, %
F61-137-1	MPCS	>230/740	12.89	3.7	100
F61-142-1	DMCS	110-136/740	31.72	2.25	3.5
F61-142-2	DMCS	136-180/740	29.22	2.50	20.0
F61-142-3	DMCS	180-202/740	21.50	3.70	25.2
F61-142-4	DMCS	119-196/144	17.45	4.80	22.9
F61-144-1 ^b	DMCS	--	27.9	2.6	--
F61-144-2 ^b	DMCS	--	22.0	3.6	--
F61-142-6	MPCS	125-200/1.25	14.0	3.3	--
F61-142-7	MPCS	200-250/1.25	7.94	6.2	--
D98-83-9	c	--	--	5	100

a Calculated from Cl analysis.

b F61-144-1 and F61-144-2 were obtained by combining appropriate fractions from two runs and redistilling.

c Prepared from octamethylcyclotetrasiloxane and DMCS.⁷

A chloro-terminated dimethylsiloxane mixture was also prepared by the reaction of equimolar quantities of octamethylcyclotetrasiloxane and DMCS, using $FeCl_3$ as catalyst, according to the method of Kambour, et al.⁷. The product (D98-83-9) was filtered to remove catalyst but was not otherwise purified. The calculated average chain length was 5 siloxane units.

The preceding siloxane intermediates were all difunctional. Some of the desired copolymers required siloxanes having either higher or lower functionality. To supply these needs, siloxanes were prepared by partial

hydrolysis of mixtures containing the monomers trimethylchlorosilane (TMCS), dimethylphenylchlorosilane (DMPS), and vinyltrichlorosilane (VCS), in addition to MPCS. The reactions including TMCS were not very successful because of the difference in reactivity between the two silanes. When the amount of water was insufficient to hydrolyze all of the chlorine atoms, most of it reacted with MPCS or VCS, and very little reaction of TMCS occurred. The unreacted TMCS distilled off with the solvent, leaving a low yield of product deficient in Cl. Runs with VCS were made at various temperatures and reactant ratios, and, in some cases, substituting DMPS for TMCS. The general procedure was similar to that previously used. The silane mixture was dissolved in THF or ethyl ether and stirred while a solution of water in THF or dioxan was added slowly. After about an hour, solvent was distilled off and the residual siloxane was heated to about 150°C. Table 5 summarizes the runs made and products obtained. The calculated functionality of the siloxanes is given as R/Si, which is the ratio of total non-hydrolyzable substituents to total Si atoms in the monomer mixture. The use of DMPS in place of TMCS gave a considerable improvement in yield and Cl content. Lowering the reaction temperature had little effect.

Another possible route to the preparation of endblocked mono-functional siloxanes is the reaction of a chlorosilane with an alkoxy silane to give ethyl chloride and a siloxane. Several experiments were done, which indicate that the reaction occurs, but that side reactions present a problem. In the reaction of trimethylethoxysilane (TMES) with MPCS in the presence of FeCl_3 , both ethyl chloride and TMCS were found in the low

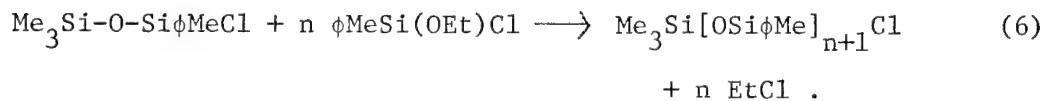
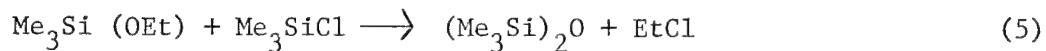
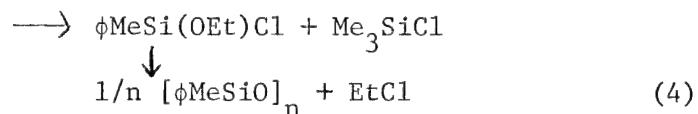
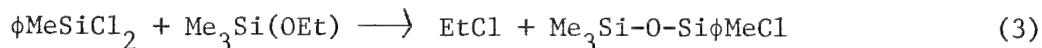
TABLE 5 - ENDBLOCKED AND MULTIFUNCTIONAL CHLOROSILOXANES

Batch No.	VCS g	moles	TMCS g	moles	MPCS g	moles	DMPS g	moles	H ₂ O g	moles	R/Si, calc.	% yield	Product			
											H ₂ O		R/Si, calc.		% yield	
											%	Cl	%	Cl	Product	
F62-22-2	--	32.6	0.3	57.3	0.3	--	5.40	0.3	2.5	58.4	5.1	14.5	79			
F62-24-1	--	32.6	0.3	57.3	0.3	--	2.70	0.15	2.5	57.9	20.4	26.8	71			
F62-27-1	--	21.7	0.2	76.8	0.4	--	7.21	0.4	2.33	73.6	3.0	9.5	96			
F62-28-1	32.3	0.2	50.8	0.47	--	6.60	0.37	2.4	38.3	5.3	18.8	61				
F62-35-2 ^a	32.3	0.2	21.7	0.2	--	5.40	0.3	2.0	25.2	7.0	18.9	67				
F62-35-1 ^a	48.5	0.3	21.7	0.2	--	7.70	0.43	1.8	38.3	10.3	18.9	82				
F62-33-2 ^a	64.6	0.4	18.6	0.17	--	9.80	0.54	1.6	50.6	11.8	18.9	94				
F62-31-1	32.3	0.2	--	57.3	0.3	--	8.60	0.48	1.6	65.3	12.8	14.0	103			
F62-32-1	32.3	0.2	10.9	0.1	38.2	0.2	--	7.70	0.43	1.8	52.9	11.7	15.3	91		
F62-32-2	24.2	0.15	16.3	0.15	28.8	0.15	--	6.10	0.34	2.0	41.5	10.9	15.8	82		
F62-32-3	16.2	0.1	--	76.4	0.4	--	7.70	0.43	1.8	69.5	11.8	12.8	100			
F62-36-1	32.3	0.2	32.6	0.3	--	5.85	0.325	2.2	29.0	--	18.8	62				
F62-37-1 ^b	16.15	0.1	--	--	39.6	0.234	3.30	0.184	2.4	54.0	9.6	10.9	118			
F62-37-3 ^b	16.15	0.1	--	--	17.0	0.1	2.73	0.15	2.0	32.6	8.5	10.9	131			
F62-37-4	32.3	0.2	--	--	14.5	0.085	4.89	0.271	1.6	34.0	12.4	14.9	107			
F62-39-2 ^b	32.3	0.2	50.7	0.467	--	6.60	0.367	2.4	31.7	3.1	18.8	50				

^a Gelled on standing.^b Cooled in Dry Ice while adding H₂O.

^c For yields below 100%, % Cl is calculated for the desired product. For yields over 100%, the extra material is assumed to be solvent, so % Cl is calculated as total Cl expected in product divided by actual weight of product obtained.

boiling fraction, and the residual product was an oil of high molecular weight and low Cl content. Apparently FeCl_3 catalyzes an interchange of chloro and ethoxy groups as well as the desired elimination of ethyl chloride. As a result of the interchange, ethoxychlorosilanes are produced, which can then eliminate ethyl chloride to give polymers, as follows:



Somewhat better results were obtained in the reaction of equimolar quantities of DMPS and MPMS. The yield of 1,1,3-trimethyl-1,3-diphenyl-3-methoxydisiloxane (F62-47-2), bp 49-50°C/0.2-0.3 mm, was 17%.

Preparation and properties of silicone-modified polyesters. -

A large number of silicone modified polyesters was prepared and evaluated. Preparations and characteristics of the various types are summarized in the following paragraphs.

Table 6 lists the compositions of the silicone-modified polyesters prepared, together with information on homogeneity, Si content, and hardness. Reactant ratios are given in terms of the ratio of hydroxy groups in the polyester to reactive groups (Cl, OR, or NH) attached to Si, and also the ratio of ST double bonds to the FU double bonds present in the polyester. Si content is given as % residue to be expected if all Si is converted to

TABLE 6 - SILICONE MODIFIED POLYESTERS

I.D. No.	Batch No.	Reactants		Reactant Ratio		% SiO ₂ , Calc.	Homogeneity	Shore Hardness
		Polyester	Silicon Compound	R-OH/ Si-X	ST/FU			
ES-1	D98-75-4, D98-77-1, D98-91-3, D98-92-3	F61-94-2	MPCS	1	1	8.8	clear	D52
ES-2	D98-77-2	F61-94-1	MPCS	1	1	5.6	clear	--
ES-3	D98-77-3	F61-94-3	MPCS	1	1	4.9	cloudy	--
ES-4	D98-77-4	F61-96-1	MPCS	1	1	3.6	cloudy	--
ES-5	D98-80-1, D98-80-5	F61-126-1	F61-137-1	1	1	18.4	clear	D50
ES-6	D98-80-2, D98-80-6	F61-126-1	MPCS	1	1	8.6	clear	D85
ES-7	D98-80-3, D98-81-1	F61-131-1	F61-137-1	1	1	10.1	cloudy	D82
ES-8	D98-81-2, D98-81-3, D98-92-1, D98-92-4	F61-131-1	MPCS	1	1	4.5	clear	D89
ES-9	D98-81-4, D98-82-4	F61-126-1	DMCS	0.5	1	16.7	cloudy	D68
ES-10	D98-81-5	F61-126-1	F61-144-2	1	1	27.0	heterogeneous	--
ES-11	D98-82-1, D98-82-5	F61-126-1	F61-142-6	1	1	20.1	clear	D45
ES-12	D98-82-2	F61-126-1	F61-142-4	1	1	31.4	heterogeneous	--
ES-13	D98-83-1, D98-84-1	F61-126-1	DMCS	1	1	9.5	opaque	D84
ES-14	D98-83-2	F61-126-1	MPMS	1	1	8.6	clear	--
ES-15	D98-83-3, D98-84-2, F62-13-1, F62-16-2, D98-92-2, D98-92-5	F61-126-1	F61-28-3	1	1	18.2	clear	D77
ES-16	D98-83-4, D98-83-8	F61-131-1	F61-28-5	1	1	30.0	heterogeneous	--
ES-17	D98-83-5	F61-126-1	F61-28-4	1	1	29.6	heterogeneous	--
ES-18	F61-146-1, D98-84-3, D98-84-4	F61-99-1	MPCS	0.5	1	10.5	heterogeneous ^a	D87
ES-19	F61-47-1	F61-99-1	F61-142-6	1	1	15.4	clear	D86
ES-20	F61-147-2	F61-99-1	F61-28-3	1	1	14.0	heterogeneous	--
ES-21	F61-153-1	F61-149-1	MPCS	0.67	0.87	5.8	clear	D89
ES-22	F61-154-1	F61-149-1	F61-142-6	0.66	0.93	15.0	heterogeneous	--
ES-23	F62-3-1	F61-151-1	MPCS	1	0.87	11.1	clear	A59
ES-24	F62-3-2	F61-149-1	MPCS	1	0.87	4.3	clear	D91
ES-25	F62-3-3	F61-155-1	MPCS	1	1.26	6.2	clear	D87
ES-26	F62-4-1	F61-151-1	F61-28-3	1.11	0.80	15.6	clear	D81
ES-27	F62-6-1	F61-155-1	DMCS	1.25	1.04	6.0	cloudy	D87
ES-28	F62-7-1	F61-150-1	F61-28-4	4.00	1.08	17.3	heterogeneous	--
ES-29	F62-8-1	F61-150-1	F61-144-1	1	1.08	18.8	heterogeneous	--
ES-30	F62-10-1	F61-150-1	MPMS	0.65	1	14.5	opaque	D82
ES-31	F62-10-3, F62-16-1	F61-150-1	DMES	1	1	12.4	clear	D82
ES-32	F62-10-4	F61-150-1	MPMS	0.37	1	17.1	heterogeneous	D40
ES-33	F62-11-2	F61-150-1	MPMS	1	1.08	11.1	clear	D84
ES-34	F62-13-2, F62-19-1, F62-19-2, F62-20-2	F61-138-1	HMDS	1	1	18.8	clear	D75-83
ES-35	F62-18-2	F62-12-1	F62-15-1	1	1.10	21.2	clear	D84
ES-36	F62-25-1	F61-138-1	MPCS	1.15	1.23	7.9	clear	D82
ES-37	F62-25-2	F61-138-1	F62-24-1	1	1.33	11.3	heterogeneous	--
ES-38	F62-26-1	F62-25-3	MPCS	1	1.49	7.8	clear	D88
ES-39	F62-31-2	F61-131-1	F62-31-1	1	5.0	13.0	clear	D88
ES-40	F62-33-1, F62-33-3	F61-131-1	F62-32-1	1	1.2	17.6	clear	D88
ES-41	F62-35-4	F61-131-1	F62-32-3	1	1.71	12.6	clear	D84
ES-42	F62-36-2	F61-131-1	F62-32-2	1	0	15.7	cloudy	D70
ES-43	F62-38-2	F61-131-1	F62-37-3	1.36	0	3.0	heterogeneous	D90
ES-44	F62-41-1	F61-131-1	F62-22-2	4.9	0.97	3.2	opaque	D87
ES-45	F62-48-3	F62-34-1	F62-47-2	1.73	1.38	9.4	clear	D83
ES-46	F62-49-2	F62-34-1	DMPS	1.23	1.09	7.9	clear	D83
ES-47	F62-49-4	F62-25-3	F62-47-2	3.26	2.11	8.2	clear	D90
ES-48	D98-98-6	F61-126-1	D98-97-4 ^b	b	b	25.1	cloudy	D88

a Formed two equal layers, which were separated and cured. Both gave clear resins, hardness D87.

b The siloxane used in ES-48 did not have Si-X groups to react with polyester OH. It contained methacrylate groups and was used in place of ST at a ratio of 1 methacrylate per FR. See Table 7 for composition.

SiO_2 and all other elements are burned to gaseous products. Hardness is given as Shore durometer readings made at room temperature on cakes of resin cured for 16 hrs at 140°C. Further evaluations of selected resins by weight loss measurements and laminate properties are discussed in subsequent sections.

Most of the silicone-modified polyesters were block copolymers prepared by heating a mixture of a difunctional hydroxy-terminated polyester and a difunctional linear siloxane (Eq. 1). The top temperature was usually about 200°C, and the reaction was continued until the evolution of volatiles stopped and the calculated weight was reached. Dichloro and dialkoxy silanes were also used to give copolymers containing one silicon atom per segment.

A second type of silicone-modified polyester is a graft copolymer prepared by the reaction of an endblocked monofunctional siloxane or silane with a polyester having hydroxy groups along the chain as well as at the ends. Several polymers of this type were prepared, although the synthetic problems previously noted cause some doubt about the identity of the siloxanes used. Monofunctional silanes such as TMCS and hexamethyldisilazane (HMDS) were also used with the same polyesters to give polyesters having side groups containing a single silicon atom.

For laminating purposes, hard, highly crosslinked resins are generally required. In these polyesters, crosslinking was achieved by copolymerization with ST, or, in ES-48, with a methacrylate siloxane. The silicone-modified polyester was dissolved in sufficient ST to give the desired ratio of ST to FU in the polyester. TBP (1% of resin weight) was added and the resin was cured for 16 hrs at 140°C. In a few cases, changes

were made in the nature of the initiator or the cure schedule, but there were no significant changes in resin properties as a result.

In general, an increase in linear siloxane content reduces the hardness of a polymer. To counteract this effect, additional functionality was incorporated in some resins through the use of siloxanes derived from VCS or 3-methacryloxypropyltrimethoxysilane (MAPS). These monomers introduce siloxane crosslinking as well as vinyl crosslinking by copolymerization with ST and FU. A few resins were also made in which difunctional siloxanes or silanes were used with polyesters containing more than two hydroxy groups per molecule to give additional crosslinking.

Two factors limited the silicone content (and hence the amount of char formation) attainable in the silicone-modified polyesters. One factor was the softening and weakening effect of siloxane linkages, especially in linear siloxanes. To some extent it was possible to counteract this effect by using siloxanes of higher functionality, as previously noted. The second factor was the tendency for polymers high in silicone to separate into two phases. In general, it was found that phenylmethyl chlorosilanes and chlorosiloxanes reacted readily to give homogeneous products, whereas dimethyl ethoxy silanes and siloxanes reacted very sluggishly to give heterogeneous materials. Basic catalysts were not effective and an acidic catalyst only partially effective in accelerating the reaction. None of the copolymers derived from a dimethylsiloxane was homogeneous, although those derived from dimethyldichlorosilane were merely cloudy and were usable. Methylphenylsiloxanes up to about the tetramer gave homogeneous products with an isophthalic-fumaric polyester. Compatibility with

straight fumaric polyesters was more limited. Both chloro and methoxy terminal groups were satisfactory. In some cases the polyester-rich phase could be cured normally to a solid resin, leaving a liquid or grease-like layer of silicone-rich material. In other cases the reaction product of polyester and silicone formed two roughly equal liquid layers when mixed with styrene. When these layers were cured, both gave hard, clear resins of about the same composition. For example, ES-18 (Table 6) formed two liquid layers, which were separated and cured individually to give D98-84-3 (upper layer) and D98-84-4 (lower layer). Both were hard and clear. Their elemental analyses (Table 7) do not differ greatly and are close to the composition calculated for complete reaction of the polyester and silicone intermediates, followed by copolymerization with the amount of ST used. In this particular case an excess of the chlorosiloxane was used, so some unreacted Cl was left in the polymer. However, the phenomenon occurred also in some of the Cl-free resins. Table 7 also includes analyses of two homogeneous polyester silicones. Compositions are close to the calculated values, although C and Si are somewhat low and O somewhat high in all cases. Apparently elimination of HCl in the condensation step was incomplete even when an excess of polyester OH was present.

Silicone-Modified Polymethacrylates

Unsaturated polysiloxanes derived from 3-methacryloxypropyl-trimethoxysilane (MAPS) were evaluated as substitutes for styrene in unsaturated polyesters and as thermosetting resins by themselves. The former approach was largely unsuccessful because of poor compatibility,

TABLE 7 - ANALYSES OF CURED SILICONE-MODIFIED POLYESTERS

	Analysis, %				
	C	H	Si	Cl	O
D98-84-3, found	61.69	5.27	4.25	6.03	21.24
D98-84-4, found	60.12	5.13	3.43	6.11	24.85
ES-18, calc.	62.90	5.63	4.92	6.21	20.33
ES-45, found	65.97	5.84	3.52	0.49	23.95
ES-45, calc.	67.51	5.95	4.39	0	22.15
ES-47, found	67.49	6.05	3.44	0.51	21.90
ES-47, calc.	69.91	5.75	3.83	0	20.51

although one such resin (ES-48) was fairly homogeneous and is listed in the preceding section. The latter approach gave a series of hard, homogeneous, thermoset polymers, which are listed in Table 8.

Various mixtures of MAPS, MPMS, and DMES were hydrolyzed with very dilute HCl and sparged at 100°C to remove most of the byproduct alcohols. The products were colorless liquids, samples of which were mixed with 1% TBP and cured for 16 hrs at 140°C.

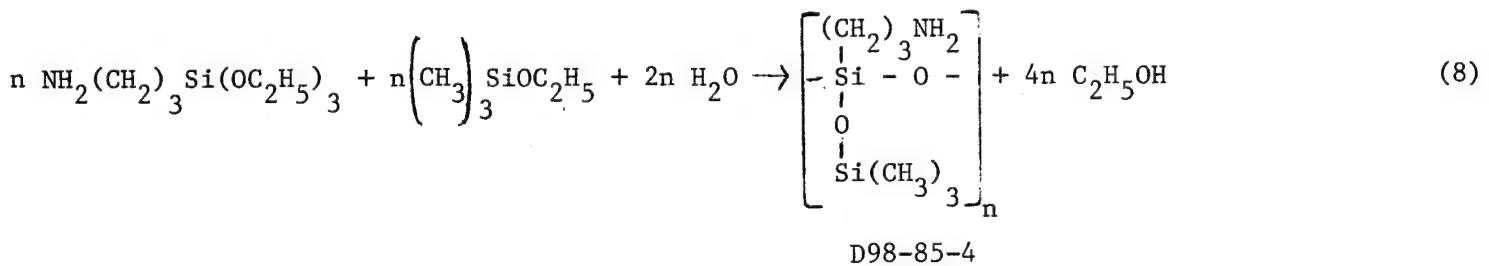
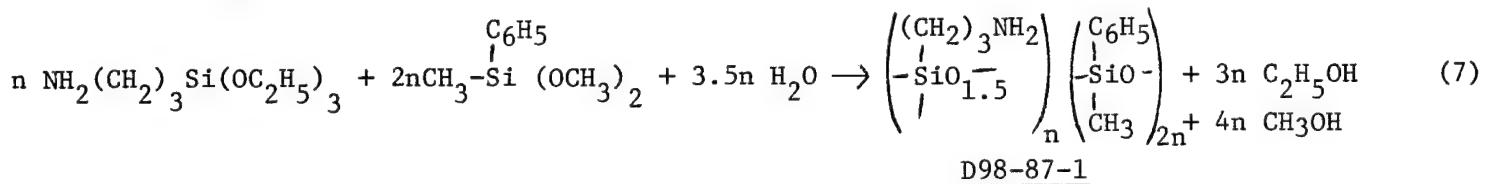
All of the compositions gave clear resins. Maximum hardness was found for polymers highest in methacrylate, with the exception of MaS-1, which had the highest methacrylate content but was relatively soft. Thick samples of the harder resins developed cracks during cure, but all of the resins were strong and tough.

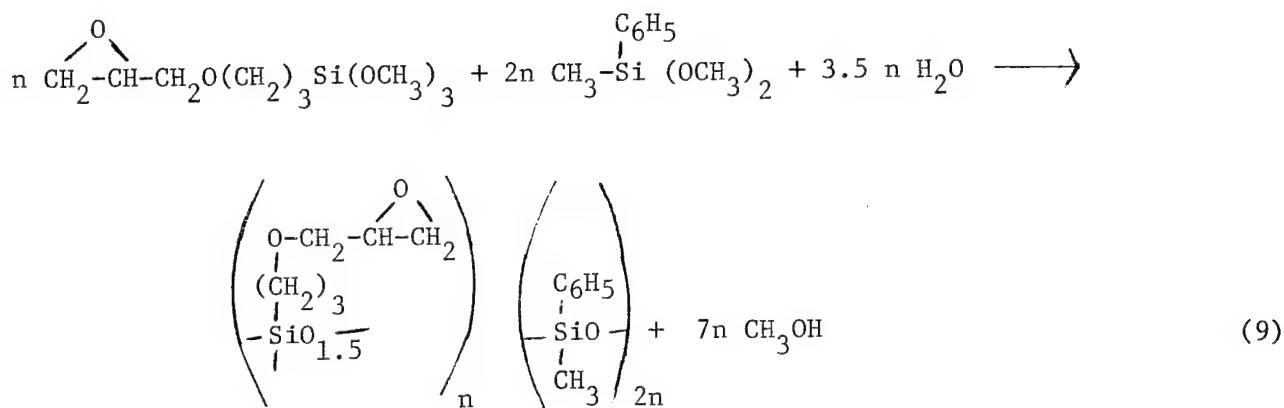
TABLE 8 - SILICONE-MODIFIED POLYMETHACRYLATES

I.D. No.	Batch No.	MAPS		MPPM		DMES		H ₂ O		Uncured Visc., Gardner	Cured Hardness, Shore	SiO ₂ %, Calc.
		g	moles	g	moles	g	moles	g	moles			
MaS-1	F62-52-3	29.8	0.12	--	--	--	--	3.6	0.31	--	30 D	33.5
MaS-2	F62-51-2	29.8	0.12	5.49	0.03	--	--	4.2	0.23	X-Y	93 D	35.2
MaS-3	F62-51-1	24.8	0.10	9.12	0.05	--	--	4.0	0.22	V-W	92 D	36.4
MaS-4	F62-50-3	24.8	0.10	18.2	0.10	--	--	5.0	0.28	V	90 D	38.1
MaS-5	{F62-50-1, F62-53-3}	12.4	0.05	18.2	0.10	--	--	3.5	0.19	N	80 D	39.9
MaS-5	{D98-97-4, D98-98-5}	24.8	0.10	36.5	0.20	--	--	6.9	0.38	--	78 D	39.9
MaS-6	{F62-50-2, F62-53-2}	9.93	0.04	29.2	0.16	--	--	4.4	0.24	M-N	80 A	41.5
MaS-7	F62-53-1	29.8	0.12	--	--	4.45	0.03	4.2	0.23	--	93 D	38.0
MaS-8	F62-52-2	29.8	0.12	--	--	8.90	0.06	4.2	0.23	H	91 D	41.7
MaS-9	F62-52-1	24.8	0.10	--	--	14.8	0.10	5.0	0.28	D-E	80 D	47.4
MaS-10	F62-51-4	19.9	0.08	--	--	23.7	0.16	5.6	0.31	<A	83 D	55.0
MaS-11	F62-51-3	12.4	0.05	--	--	29.7	0.20	5.5	0.30	<A	65 D	63.1

Silicone-Modified Epoxies

Synthetic plan. - The organosilicon monomer 3-glycidoxypropyltrimethoxysilane (GPS) was used as a source of epoxy functionality, and the monomer 3-aminopropyltriethoxysilane (APS) was used to provide epoxy curing capability. The siloxane functionalities of APS and GPS were reduced by copolymerizing them with monomers of lower functionality in order to minimize problems of insolubility and premature gelation. The degree of siloxane crosslinking possible in the fully cured copolymers is conveniently expressed as the R/Si ratio, which is the total number of non-hydrolyzable groups attached to silicon divided by the total number of silicon atoms. An R/Si value of 2 corresponds to a linear polymer with no intentional endblocking. Values higher than 2 characterize endblocked linear materials, and values lower than 2 give materials which are crosslinked and thermoset when fully cured. The following reactions illustrate the kinds of siloxanes prepared:



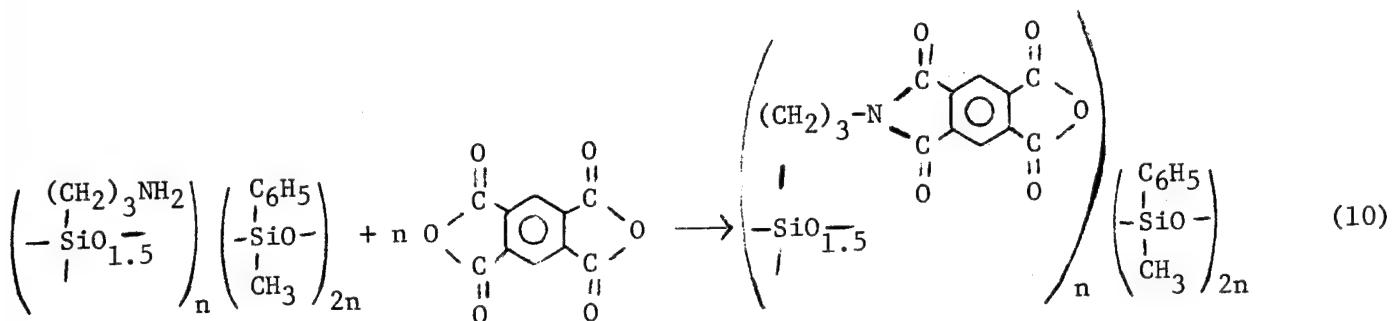


D98-93-1

These equations are idealized. Under the gentle hydrolysis conditions employed, some alkoxy and silanol groups would be present in the polymers and act as endblocking groups. On the other hand, in eq. 8 a portion of the trimethylethoxysilane (TMES) would self-condense to hexamethyldisiloxane, which would volatilize, leaving a product with a functionality higher than calculated.

D98-87-1 and D98-85-4 are aliphatic polyamines, which are effective epoxy curing agents at room temperature. They and related siloxanes were used to cure both epoxy siloxanes, such as D98-93-1 and a commercial liquid epoxy, Epon 828 (E8), which consists primarily of the diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane.

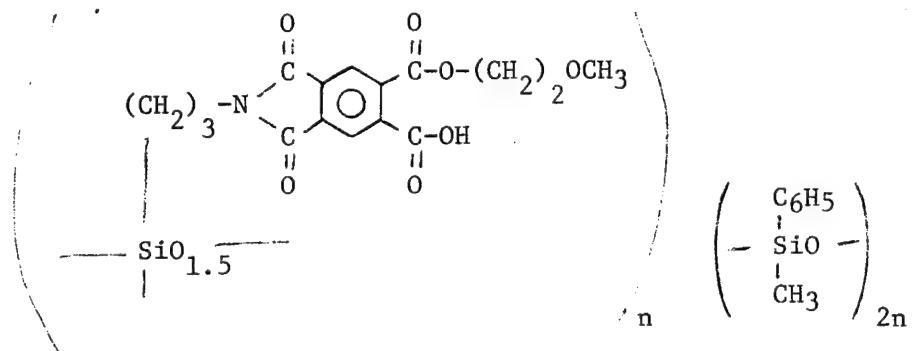
D98-87-1 was also converted to an anhydride by reaction with pyromellitic dianhydride (PMDA):



D98-95-4

D98-95-4 is a polyanhydride, and was found to be an effective high-temperature curing agent for E8 and for D98-93-1. Other aromatic anhydrides, such as 3,4,3',4'-benzophenonetetracarboxylic dianhydride (BTDA), PMDA and trimellitic anhydride (TMA) were also used to cure D98-93-1.

D98-95-4 was also esterified with 2-methoxyethanol (MOE) to give



D98-108-1

The esterified material was a somewhat less reactive epoxy curing agent than D98-95-4. It was used to cure both E8 and D98-93-1.

Amine cured epoxies. - Cohydrolysis of APS and TMES was conducted at room temperature by adding the calculated amount of water for complete hydrolysis to a mixture of the monomers. The mixture was stirred

intermittently at room temperature, and the following changes were observed: two colorless, immiscible liquids \xrightarrow{A} clear, colorless solution (possibly a microemulsion) \xrightarrow{B} cloudy liquid, slowly separating into two liquid phases \xrightarrow{C} colorless, homogeneous liquid. Results are given in Table 9.

TABLE 9 - COHYDROLYSIS OF APS AND TMES

Batch No.	R/Si	APS		TMES		H_2O		Approx. Time, Mins		
		g	moles	g	moles	g	moles	A	B	C
D98-85-1	1.4	11.07	0.05	1.48	0.0125	2.9	0.16	1	1	15
D98-85-2	1.6	11.07	0.05	2.54	0.0215	3.1	0.17	1.5	1	20
D98-85-3	1.8	11.07	0.05	3.94	0.0333	3.3	0.18	2	1	25
D98-85-4	2.0	11.07	0.05	5.92	0.05	3.6	0.2	2.5	1	60
D98-85-5	2.2	8.86	0.04	7.10	0.06	3.3	0.18	3	1	75
D98-85-6	2.4	6.64	0.03	8.27	0.07	2.9	0.16	4	1	130
D98-85-7	2.5	6.64	0.03	10.65	0.09	3.3	0.18	5	1	160

A portion of each of the products from Table 9 was mixed with E8 at a ratio of two epoxy groups per amino group. None of the mixtures was homogeneous, so 10 ml of toluene was added to each to give a cloudy suspension. The samples were baked for 65 hrs at 60°C to give clear hard resins, which were baked further for 2 hrs at 140°C to give the products of Table 10.

Although the original mixtures were not compatible at room temperature, even with the addition of a mutual solvent, the cured resins were clear. Those having the highest R/Si values were hard on the top, but soft on the bottom. Their weights were also a lower percentage of the calculated value than were those of the samples having lower R/Si values.

TABLE 10 - SILICONE-MODIFIED EPOXY RESINS FROM E8
AND AMINOPROPYL SILOXANES

I.D. No.	Batch No.	Siloxane*		% SiO ₂ Calc.	Weight g	Cured Product	
		No.	g			% of Calc.	Hardness, Shore D
Eps-1	D98-89-1	D98-85-1	4.635	11.1	7.60	102	75
Eps-2	D98-89-2	D98-85-2	5.01	12.2	7.53	98	85
Eps-3	D98-89-3	D98-85-3	5.49	13.7	8.12	102	70
Eps-4	D98-89-4	D98-85-4	6.18	15.4	8.03	96	80
Eps-5	D98-89-5	D98-85-5	7.23	17.8	8.37	93	70
							Top hard, tough; bottom soft, gummy.
Eps-6	D98-89-6	D98-85-6	8.91	20.8	8.52	86	80
Eps-7	D98-89-7	D98-85-7	10.29	22.7	8.57	80	70

*In all cases 5.55 g (0.03 mole epoxide) of E8 was used, with enough siloxane to give 0.015 mole of amino group.

These two effects are probably due to the production of hexamethyldisiloxane as a byproduct. Part of it volatilized during cure to give a lower weight than predicted; part was trapped in the lower part of the sample and plasticized it.

Compatibility of the compositions was also investigated in the absence of solvent. The mixtures of Table 10 were made again, omitting the toluene. They were warmed in a bath of boiling water. All became clear and homogeneous and then gelled. The time for gelation varied from about 15 secs for D98-89-1 to about 3 mins for D98-89-7.

A similar hydrolysis procedure was used to prepare a siloxane from a mixture of 2 moles of MPMS and 1 mole of APS. The product was a clear, colorless liquid (D98-87-1), which was mixed with E8 at a ratio of 2 epoxy groups per amino group to give a homogeneous liquid (D98-87-2). A small sample of this product, heated to 50°C, gelled in 15-20 mins. Another sample, stored at room temperature, gelled in about 90 mins. A third sample was cured as shown in Table 11 to give a resin (EpS-8) yielding 23.8% SiO₂ (calc.).

D98-87-1 was also used to cure a glycidoxyl siloxane polymer, prepared by cohydrolysis of 2 moles of MPMS and 1 mole of GPS. The uncatalyzed hydrolysis reaction was less rapid than those involving APS, so a trace of HCl was used to obtain a satisfactory reaction rate at about 75°C. The product was a colorless liquid (D98-93-1), which was mixed with D98-87-1 at an epoxy/amine ratio of 2 to give a clear, colorless liquid (D98-87-4) of low viscosity. Gel time for this material at room temperature was between 4 and 20 hrs.

TABLE 11 - CURE OF SILICONE EPOXY RESIN EpS-8
(Batch D98-90-1)

Cure Schedule ^a		Weight		Appearance
Time Hrs.	Temp., °C	g	% of Calc. ^b	
0	25	20.00	135	Colorless liquid.
0.17	50	--	--	Tacky gel.
2.0	50	--	--	Firm, flawless, non-tacky.
3.0	50	19.14	129	Firm, flawless, non-tacky.
0.5	100	17.78	120	Firm, many bubbles.
2.5	100	15.57	105	Hard, many bubbles.
18.5	100	15.26	103	Hard, many bubbles.
22.5	100	15.26	103	Hard, many bubbles.
42.5	100	15.21	103	Hard, many bubbles.
8.0	150	14.97	101	Clear brown. Cracked. Shore D86.

a - Times at each temperature are totals for that temperature. Total cure is sum of cures at each temperature.

b - Calculated weight assumes complete conversion of ethoxysilanes to siloxanes.

Two samples of D98-87-4 were placed in aluminum dishes and cured simultaneously under the same conditions. One sample (D98-90-2) weighed 20.00 g and had an initial thickness of about 9 mm. The second sample (D98-90-3) weighed 10.00 g and had an initial thickness of about 4.5 mm. The cure schedule and results are shown in Table 12.

TABLE 12 - CURE OF SILICONE EPOXY RESIN EpS-9
(Batch D98-87-4)

Cure Schedule, Hrs/°C	Sample D98-90-2			Sample D98-90-3		
	Wt., g	Wt., % of Calc.	Appearance	Wt., g	Wt., % of Calc.	Appearance
0.67/60	17.06	133	Tacky gel	8.06	117	Partial gel
2/60	16.65	130	Firm gel	7.67	111	Firm gel
18/60	13.58	106	Hard, bubbles and cracks	6.92	100	Hard, few bubbles
26/60	13.52	106	Same	6.81	99	Same
26/60 + 16/100	13.26	104	Same	6.64	96	Same
26/60 + 16/100 + 8/150	12.92	101	Same	6.51	94	Same
26/60 + 16/100 + 24/150	12.80	100	Same, Shore D70	6.41	93	Same, Shore D70

The fully cured resins had thicknesses about 60% of their initial values. They were clear amber. D98-90-2 had a layer of small bubbles on the bottom and had several large cracks. D98-90-3 had only a few bubbles and a few small cracks at the edges. Calculated yield of SiO_2 is 42.8%.

Elemental analyses of cured resins (Table 13) confirm the expected loss of Si from siloxanes prepared from mixtures high in TMES. Those derived largely from other monomers gave analyses close to the calculated values. The analyses of D98-90-2 and D98-90-3 suggest that D98-90-3, which was the thinner of these two samples of the same material, underwent some oxidation of alkyl groups during cure.

TABLE 13 - ANALYSES OF EPOXY SILICONES

Sample	Analysis, %				
	C	H	N	O	Si
D98-89-1, found	61.70	7.53	2.75	17.66	7.76
	63.77	7.32	2.80	19.09	7.01
D98-89-4, found	64.90	7.21	1.90	16.96	8.41
	61.67	7.74	2.50	18.09	10.01
D98-89-7, found	64.88	7.04	2.35	16.70	8.02
	57.79	8.51	1.94	16.24	15.52
D98-90-1, found	63.51	6.66	1.86	15.72	10.80
	63.63	6.71	1.85	16.70	11.11
D98-90-2, found	55.13	6.40	1.12	17.39	19.50
D98-90-3, found Calc. for D98-90-2 or D98-90-3	53.98	6.14	1.21	20.02	18.44
	54.25	6.23	1.11	18.38	20.03

Anhydride cured epoxies. - Table 14 lists the anhydride cured silicone modified epoxy resins that were prepared. When EpS-10 or EpS-11 was prepared by warming a mixture of PMDA and D98-93-1, the PMDA dissolved at about 120°C to give a clear solution. The solution rapidly increased in viscosity and became a soft gum, largely soluble in THF. A 20% solution of the starting materials in THF was then refluxed for 9 hrs with little change in viscosity. When the solution was boiled down it became cloudy at 73% solids, and a precipitate formed on cooling. Apparently there was little reaction with PMDA under these conditions. Other solvents evaluated for use with EpS-11 were dimethylformamide (DMF), 1,2-dimethoxyethane (DME), and 2-ethoxyethyl acetate (EEA). Clear solutions at room temperature were obtained only with DMF, which is difficult to remove without blistering during cure. Better results were obtained by esterifying the PMDA with MOE and using additional MOE as a solvent. A clear, stable solution was obtained (EpS-11E), which cured more slowly than EpS-11 and had less tendency to cause blistering of laminates than non-esterified solutions containing DMF.

Results with BTDA cure of D98-93-1 were similar. When heated without solvent, the mixture gelled before the BTDA dissolved completely. The use of solvents gave results similar to those obtained with PMDA, the reactive solvent MOE being the most satisfactory (EpS-12E). TMA was investigated only briefly as a curing agent. When heated with D98-93-1, it gave about the same behavior as PMDA. Solvents were not studied.

D98-95-4 was prepared by slow addition of freshly prepared D98-87-1 to a rapidly stirred solution of PMDA in warm THF. A clear,

TABLE 14 - ANHYDRIDE CURED SILICONE MODIFIED EPOXIES

I.D. No.	Batch No.	Reactants		Reactant Ratio, Anh./Epoxy	% SiO ₂ , Calc.	Shore Hardness ^a
		Epoxy	Cure			
EpS-10	D98-93-4, D98-94-1	D98-93-1	PMDA	0.6	35.7	D80
EpS-11	{ D98-94-2, F32-45-3, F32-78-2	D98-93-1	PMDA	0.85	33.9	D82
EpS-12	D98-95-2	D98-93-1	BTDA	0.85	31.2	D80
EpS-13	D98-95-3, F32-45-4	D98-93-1	TMA	0.57 ^b	33.2	D80
EpS-14	D98-110-1	D98-93-1	PMDA diester ^c	0.85 ^c	33.9	--
EpS-15	D98-110-3	D98-93-1	BTDA diester ^c	0.85 ^c	31.2	--
EpIS-1	{ D98-96-1, F32-53-1, F32-67-1	E8	D98-95-4	0.85	22.5	D85
EpIS-2	{ D98-96-2, F32-46-8, F32-58-3, F32-61-2	D98-93-1	D98-95-4	0.85	35.7	D75
EpIS-2A	F32-75-1	D98-93-1	D98-95-4	0.91	35.5	--
EpIS-1E	D98-109-2	E8	D98-108-1	0.85 ^c	22.5	--
EpIS-2E	D98-111-2	D98-93-1	D98-108-1	0.85 ^c	35.7	--

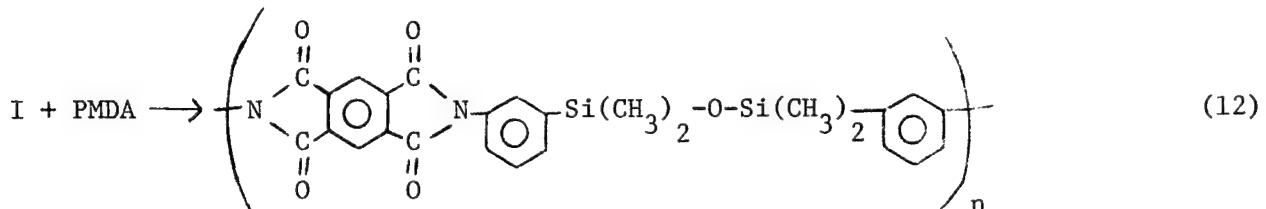
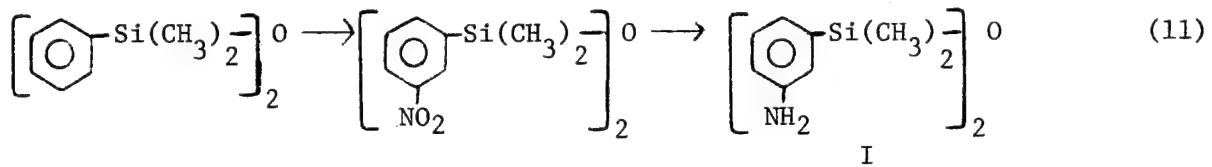
^a Samples cured 2 hrs at 120°C and 3 hrs at 200°C.^b TMA contains a CO₂H group also, so the combined functionality toward epoxy is equivalent to an anhydride/epoxy ratio of 0.85.^c MOE added as solvent and to form carboxy ester anhydride groups.

colorless solution was obtained, which was stable at room temperature. However, if the D98-87-1 was allowed to stand for a day after its preparation, it gave a precipitate with the PMDA solution, and a clear solution could not be obtained. Blends of D98-95-4 with E8 (EpIS-1) or with D98-93-1 (EpIS-2) were clear and could be boiled down to about 75% solids in THF without gelation. DMF and EEA were also used successfully as cosolvents. The use of MOE as an esterifying solvent gave good results, with reduced blistering (EpIS-1E and EpIS-2E).

Silicone-Modified Polyimides

Three types of silicone-modified polyimides were investigated. One type also incorporated epoxy groups and was discussed in the preceding section (EpIS-1 to EpIS-2E). A second type was prepared by the reaction of a dianhydride with a diamino siloxane. The third type was prepared by the PMR method from a polyaminopolysiloxane and esters of BTDA and 5-norbornene-2,3-dicarboxylic anhydride (NBA).

A polymer of the second type was prepared by the following reaction sequence:



Nitration of 1,3-diphenyltetramethylidisiloxane was attempted with fuming HNO_3 in acetic anhydride and CH_2Cl_2 ⁹, with $\text{Cu}(\text{NO}_3)_2$ in acetic anhydride¹⁰, and with $\text{Cu}(\text{NO}_3)_2$ in acetic anhydride and tetramethylene sulfone. None of the methods gave a pure product, but the crude nitro compounds were hydrogenated with Pd-on-C to give a mixture of amines. Attempts to purify the diamine were unsuccessful, but a polymer was prepared from PMDA and the crude material. The polymer gave a brittle film and appeared to be of low molecular weight. This approach was discontinued in favor of the PMR method, which was more successful and gave polymers of higher Si content.

Five silicone-modified polyimides were prepared by an adaptation of the PMR method of Serafini, et al.¹¹, using an aminopropyl siloxane and ethyl esters of BTDA and NBA. A 0.4 molar solution of the diethyl ester of BTDA was prepared by refluxing BTDA and ethanol for 2 hrs. An 0.8 molar solution of the monoethyl ester of NBA was prepared in the same way except that a 40/60 THF/ethanol mixture was used to keep the ester in solution. The aminopropyl siloxane (batch D98-105-2) was prepared by the hydrolysis of 2 moles of MPMS and 1 mole of APS and was identical to D98-87-1 (eq. 7). Mixtures of D98-105-2 with the two ester solutions were made to give the compositions shown in Table 15. The solutions were boiled down at 100°C to viscous liquids, which were cured for 6 hrs at 110°C and 18 hrs at 200°C to give hard tough resins. All of the samples contained large bubbles, which made it difficult to measure hardness, but all of the values were in the range of 80-85 Shore D. The high yields indicate that there was not an excessive loss of cyclopentadiene in the cure, although the samples were baked in open dishes.

TABLE 15 - SILICONE-MODIFIED PMR POLYIMIDES
FROM APS-MPMS₂ COPOLYMER

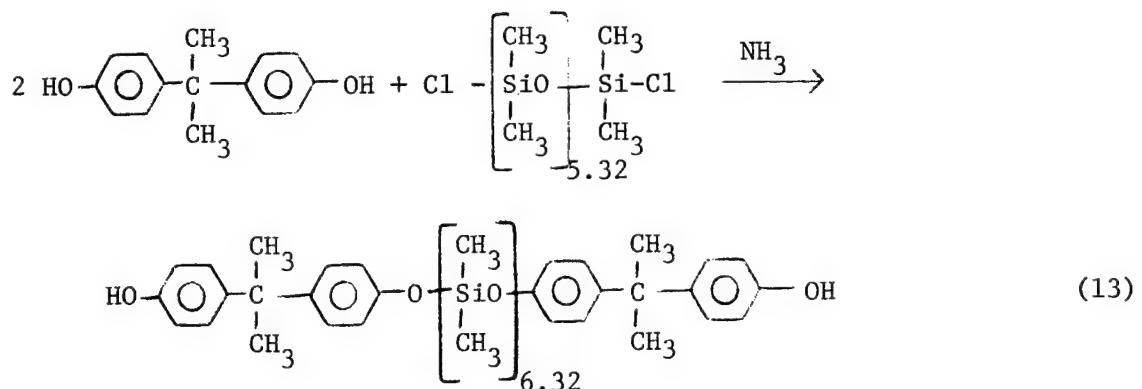
I.D. No.	Batch No.	Mole Ratio, BTDA/NBA/NH ₂	Yield, %	% SiO ₂	Shore Hardness	<u>n</u> ^a
IS-1	D98-107-1	1/2/4	98	34.2	D80-85	1.0
IS-2	D98-107-2	1.1/2/4.2	98	34.2	D80-85	1.1
IS-3	D98-107-3	1.3/2/4.6	99	34.2	D80-85	1.3
IS-4	D98-107-4	1.6/2/5.2	99	34.2	D80-85	1.6
IS-5	D98-107-5	2/2/6	96 ^b	34.2	D80-85	2.0

a Composition expressed as n moles BTDA + (2n + 2) equiv. NH₂ + 2 moles NBA.

b Includes some mechanical loss.

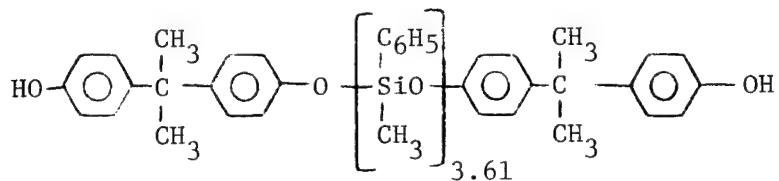
Silicone-Modified Phenolic Resins

A silicone-modified phenolic intermediate was prepared by a modification of the method of Kambour, et al.⁷, using the reaction:



D98-100-3

A second intermediate, made similarly from a methylphenyl dichlorosiloxane, had the approximate structure:



D98-100-6

The siloxane intermediate (D98-83-9) used in the preparation of D98-100-3 was made by the reaction of DMCS with octamethylcyclotetrasiloxane, and the intermediate (D98-100-4) for D98-100-6 was made by partial hydrolysis of MPCS. Both methods are discussed in an earlier section.

Attempts to prepare a resole from D98-100-6 and paraformaldehyde under relatively anhydrous conditions, using benzyltrimethylammonium hydroxide as catalyst, were unsuccessful. THF and DMF were used as solvents, with reaction temperatures up to 130°C. Products were baked at temperatures up to 175°C both with and without acidic catalysts to give, in most cases, two liquid layers.

D98-100-3 and D98-100-6 were cured successfully with hexamethylene-tetramine (HXA). Various mixtures of powdered HXA and the two phenolic siloxanes were baked at 150°C and 200°C to give the products of Table 16.

TABLE 16 - SILICONE-MODIFIED PHENOLIC RESINS

I.D. No.	Batch No.	Phenolic Siloxane	HXA, Wt. %	% SiO ₂ Calc.	Shore Hardness	
					1 hr/150°C	7 Hrs/200°C
PS-1	D98-103-2	D98-100-3	4	47.5	A55	D40
	D98-103-3	D98-100-3	8	46.4	A73	D69
	D98-103-4	D98-100-3	12	45.6	A75	D73
PS-2	D98-103-5	D98-100-6	4	23.3	D59	D75
	D98-103-6	D98-100-6	8	22.9	D78	D80
	D98-103-7	D98-100-6	12	22.5	D79	a

a Bubbles prevented measurement.

All of the fully cured resins were hard, black, and full of bubbles.

Weight Loss Determinations

TGA. - Thermogravimetric analyses (TGA) of neat specimens of selected resins were made, using a Perkin-Elmer TGS-2 Thermogravimetric System. Samples of about 5 mg were heated to 1,000°C at rates of 5°C/min and 80°C/min in air and in N_2 at a flow rate of 100 cc/min. This wide range of conditions was employed to simulate as well as possible the range of heating rates and oxidizing-reducing atmospheres encountered in a fire.

The TGA results are summarized in Table 17. All of the polyesters gave residue weights well below the weight calculated for SiO_2 , whereas most of the other polymers had average residues higher than the calculated value. The low values presumably occurred because of loss of Si in the form of volatile cyclic siloxanes or glycol silicates. Somewhat higher average results might have been obtained if more polyesters had been run in N_2 , but work on the other systems was considered more valuable. Char yields higher than the calculated SiO_2 values indicate retention of carbon, presumably as highly condensed aromatic structures and possibly some SiC. The highest char/ SiO_2 ratios occurred in N_2 and with polymers high in aromatic groups.

Isothermal weight loss. - Weight loss measurements of neat samples of eight silicone-modified resins were made in forced draft ovens at three temperatures. The samples consisted of broken pieces of resin, 2-3 mm thick, weighing approximately 0.5 g each. Two samples of each resin were run. The results are summarized in Table 18.

TABLE 17 - THERMOGRAVIMETRIC ANALYSES OF SILICONE-MODIFIED POLYMERS

I.D. No.	Calc. SiO ₂ , %	Residual Char at 1,000°C, %				Ratio, Av. Char/ Calc. SiO ₂	
		Air		N ₂			
		5°C/min	80°C/min	5°C/min	80°C/min		
ES-1	8.8	2.8 ^a	5.0	2.1	1.9	0.34	
ES-2	5.6	1.6 ^a	1.1 ^a	--	--	0.24	
ES-3	4.9	1.3 ^a	0 ^a	--	--	0.13	
ES-4	3.6	0.8 ^a	0.4 ^a	--	--	0.17	
ES-7	10.1	--	0 ^a	--	--	0	
ES-8	4.5	2.0	0.9	2.1	6.7	0.65	
ES-11	19.5	5.4 ^a	4.8	--	--	0.26	
ES-15	19.7	6.5	4.9	--	--	0.29	
ES-48	25.1	20.0	15.4	26.6	22.7	0.84	
MaS-5	42.9	33.0	31.3	33.4	30.3	0.75	
EpS-1	11.1	17.6	12.2	--	--	1.34	
EpS-4	15.4	17.1	27.8	30.1	26.9	1.65	
EpS-7	22.7	10.0	18.0	--	--	0.62	
EpS-8	23.7	23.0	35.9	40.2	41.4	1.48	
EpS-9	42.8	37.8	41.0	42.1	40.6	0.94	
EpS-10	35.7	33.5	36.0	43.3	35.7	1.04	
EpS-11E	33.9	31.4	29.2	36.9	32.9	0.96	
EpS-12E	31.2	27.2	23.8	37.3	33.7	0.98	
EpS-13	33.2	28.9	25.5	--	--	0.82	
EpIS-1	22.5	20.1	38.2	45.0	43.5	1.63	
EpIS-2	35.7	32.3	44.1	49.6	48.4	1.22	
EpIS-1E	22.5	18.4	19.2	40.7	40.3	1.32	
EpIS-2E	35.7	31.5	21.0	63.1	57.6	1.21	
IS-1	34.2	32.1	31.4	56.4	48.9	1.23	
IS-5	34.2	32.4	30.6	57.0	51.6	1.25	
PS-1	46.4	35.9	28.5	48.9	44.6	0.85	
PS-2	22.9	22.6	21.0	63.1	57.6	1.79	

a - Maximum temperature 800-900°C.

TABLE 18 - ISOTHERMAL AGING OF NEAT RESINS

I.D. No.	Weight Loss, %						Rate of Loss, Last Period, % Per 100 Hrs		
	96 Hrs		144 Hrs		192 Hrs		175°C	200°C	225°C
	175°C	200°C	175°C	200°C	175°C	200°C	225°C	175°C	200°C
EpIS-1	1.1	3.0	10.5	1.4	4.0	13.6	1.7	5.0	16.4
"	1.0	3.0	12.6	1.3	3.8	16.8	1.5	4.9	20.5
EpS-11	7.4	12.2	22.9	8.8	14.6	26.6	10.0	16.5	29.3
"	7.8	12.9	23.1	9.1	15.4	26.9	10.3	17.3	29.5
EpS-13	7.5	12.2	18.4	8.8	14.3	21.4	9.8	15.8	23.6
"	8.2	11.5	18.4	9.6	13.5	21.5	10.4	15.1	24.3
ES-45	5.1	10.0	19.9	6.4	12.1	23.4	7.7	13.6	26.4
"	5.6	10.1	19.6	7.0	12.2	23.3	8.0	13.8	26.3
EpS-10	4.5	9.4	20.4	5.8	12.3	24.5	6.9	14.4	27.0
"	4.5	8.7	20.9	5.5	12.0	24.5	6.4	14.3	27.3
EpIS-2	2.6	8.0	15.6	3.2	10.0	18.2	4.0	11.3	20.2
"	2.7	7.3	13.9	3.3	9.3	16.6	4.3	10.6	18.7
MaS-5	4.1	6.2	12.3	4.6	6.8	15.2	5.0	7.3	17.8
"	4.8	5.6	13.1	5.3	6.3	15.9	5.6	6.7	18.4
Eps-12	3.3	6.3	13.1	3.9	7.5	17.0	4.6	8.3	19.9
"	3.7	6.1	15.5	4.2	7.1	17.9	4.7	7.7	20.2

In determinations of this sort the initial part of the weight loss may include loss of solvent, moisture, or products of condensation, which are not related to the thermal stability of the resin itself. For this reason the rate of weight loss in the latter part of the determination may be more indicative of thermal stability than the total weight loss. Average rates of loss during the final portion of the aging period are also included in Table 18.

The following four resins were superior to the other four in weight retention at all three temperatures and in final slope at 175 and 200°C: EpIS-1, EpIS-2, MaS-5, and EpS-12.

GRAPHITE FIBER LAMINATES

As a preliminary, small-scale evaluation, several of the resins were used to impregnate Hexcel style 3T716 graphite fabric. In this fabric, unidirectional graphite fibers are held together by glass fibers running perpendicularly across the graphite fibers. Approximately 5" x 5" sheets were laid on a sheet of Mylar, a small portion of resin solution was added to the sheet, another sheet of Mylar was placed on top, and the resin was worked around with a doctor blade. The sheets were B-staged at the conditions given in Table 19. The samples were then cut into 4" x 4" sheets and laminated. The laminating layup included 4 sheets of B-staged fabric placed between 2 sheets of heavy aluminum foil which had been sprayed with M/S 122 release agent, and this package placed between 2 steel plates. Laminating conditions are also given in Table 19.

TABLE 19 - GRAPHITE FABRIC LAMINATES

I.D. No.	Laminate No.	Pre cure		Press Conditions		Flexural Properties	
		Time, Min	Temp., °C	Time, Min	Temp., °C	Pressure, psi	Strength, ksi
EpS-8	F32-54-3	5	80	60	110	500	75
EpS-8	F32-54-4	2	80	60	110	500	88
EpIS-1	F32-53-2	1	100	30	140	750	112
EpIS-1	F32-53-3	4	65	30	140	500	105
EpS-11	F32-46-5	5	110	20	160	750	103
EpIS-2	F32-46-10	5	105	30	140	630	53
MaS-2	F62-56-4	none		30	140	600	b
MaS-5	F62-72-2	2 ^a	250	45	200	900	54
MaS-8	F62-57-2	none		60	140	600	b
							b

a - Pre cure for this laminate was in two steps, as shown. It was also postcured for 18 hrs at 200°C.

b - Flexural properties were not determined, but the laminates were hard and well consolidated.

The 4" x 4" laminates were cut into test specimens 1" x 2". Thicknesses varied from 0.023" to 0.034". Flexural strength and modulus were determined, using a span length of 1" and a test speed of 0.05"/min. Each of the values in Table 19 is the average of two determinations.

Laminates were fabricated on a larger scale from prepreg prepared by filament winding. A McClean-Anderson Model W-1 filament winding machine was set up with a mandrel having a length of 30" and a diameter of 13". The mandrel was covered with Daubert Release Paper 2-65-KG-1. The gears were set up for circumferential winding with an initial band width of 0.15". This means that the head directing the fiber onto the mandrel is moved 0.15" for each revolution of the mandrel. This setting provides for a slight overlapping of the fiber so as to obtain a continuous sheet of impregnated fiber.

The roll of fiber (Hercules AS-4) was placed on a device that allowed it to unroll with a small amount of tension. The fiber strand was threaded through the resin pan, under a 6" dia. roller, out through an adjustable wiper, across a small roller, and then through a guide onto the revolving mandrel. The resin pan, wiper, rollers, etc., are all one unit, which moves in a direction parallel to the axis of the mandrel. The amount of resin build can be varied by adjusting the wiper, but in most cases it was necessary to adjust the viscosity and concentration of the resin solution by the addition of solvent in order to obtain the desired resin content in the prepreg. Solvents which were found suitable for the purpose were THF, DMF, and 2-ethoxyethyl acetate (EEA).

After the mandrel was covered with impregnated fiber, resistance heaters were moved up next to the revolving mandrel. The temperature of the coated fiber was adjusted by placing the heaters at various distances from the mandrel, and was estimated by placing a thermometer close to the mandrel. Times and temperatures for this step given in Table 20 refer to total heating time and maximum temperature observed. In general, the operation began at room temperature. The temperature was raised gradually by moving the heaters progressively closer until the temperature reached the value given. The thermal conditions in this step were not well defined, and the primary criterion of suitable pre-cure was the physical state of the prepreg (tack, flexibility, coherence, etc.). When the prepreg approached a tack-free state, it was cut from the mandrel and pressed into fairly flat pieces. In some cases additional pre-cure in an oven was given to the cut pieces.

The sheets of prepreg were cut into 4" x 4" squares, stacked with the fibers parallel, and placed in a steel mold to prevent the fibers from being squeezed out at the edges when pressed. The assembly was placed in the press. Pressure was applied, and the temperature raised and held for a suitable time. Laminates were removed from the press and postcured in an oven. Processing conditions and properties of laminates are summarized in Table 20. Flexural strength and modulus were determined in accordance with ASTM D790 and interlaminar shear strength in accordance with ASTM D2344. Resin content of prepgs or laminates was estimated from the formula

$$\% \text{ resin} = \left(\frac{W - 0.0223 \frac{A}{P}}{\frac{W}{P}} \right) \times 100,$$

TABLE 20 - FILAMENT WOUND 4" x 4" GRAPHITE LAMINATES

Resin I.D. No.	Laminate No.	Press Conditions				Postcure Hr.	Thickness, Mils	Wt. % Resin	Flexural Properties ^a		Interlaminar Shear Strength, kpsi 25°C 200°C	Resin Density, g/cc	Fiber Volume, %	Void Volume, %	
		Precur- Min Man	Precur- Max Man	psi	Min				25°C	200°C					
Eps-11E	F62-102-2	55 ^c	280 ^c	630	150	25	225	0.75	250	116	36	—	—	5.5	2.5
Eps-11E	F62-103-1	47	270	500	45	150	225	0.75	235	97	32	—	—	60	2.7
Eps-11E	F62-103-2	54	225	630	105	150	225	265	250	104	35	—	—	—	—
Eps-11E	F62-103-4	47 ^c	225 ^c	630	70	25	225	—	—	83	22	—	—	22	—
Eps-11E	F62-104-1	54 ^c	225 ^c	630	120	160	225	—	—	100	34	24.4	9.1	2.1	1.27
Eps-12	F62-84-1	20	160	1,300	75	25	225	—	—	105	34	74	—	1.86	0.65
Eps-12	F62-84-1	20	160	1,300	105	225	225	4	200	115	38	88	—	1.55	1.27
Eps-12	F62-84-1	20	160	1,300	80	225	225	4	200	101	33	67	—	—	—
Eps-12	F62-84-2	20	160	1,300	85	25	225	2	200	105	33	78	—	1.54	0.62
Eps-12	F62-70-1	20	80	880	30	25	160	62	225	37	30	180	—	5.0	—
Eps-12	F62-71-3	20	80	880	55	25	175	—	—	47	36	110	—	—	—
Eps-12	F62-80-1	15	70	630	60	25	225	4	200	98	35	71	—	4.9	—
Eps-12	F62-106-2	20	75	630	120	170	225	—	—	109	32	46	7.2	9.1	—
Eps-1E	F62-106-4	10	150	630	120	25	225	—	—	31	—	—	—	1.55	1.27
Eps-1E	F62-83-1	8	160	630	120	25	225	4	200	90	34	98	—	3.5	0.91
Eps-1E	F62-83-2	8	160	630	100	25	225	4	200	109	38	74	—	4.7	—
Eps-1E	F62-83-3	8	160	630	120	25	225	4	200	106	36	104	—	—	—
Eps-2E	F62-107-3	20	70	630	150	225	225	—	—	—	—	—	—	—	—
Eps-2E	F62-106-1	20 ^c	75 ^c	630	90	170	225	—	—	105	32	31	—	3.0	0.98
Eps-2E	F62-106-3	10	150	630	75	25	225	1	250	—	38	31	—	3.2	0.91
Eps-2E	F62-111-1	10	80	1,300	1,000	225	225	—	—	92	—	—	—	1.53	1.26

^a Average of 2-5 samples.^b Estimated from ultrasonic C scan.^c Additional oven precurse of 2 mins at 180°C.

in which W_p is the weight in g of prepreg or laminate, A_p is the area of the prepreg in sq. in., and b is the filament winding band width in inches. The factor 0.0223 is the weight of the untreated fiber in g/in. Densities of neat resins were determined by ASTM D792-B, and of laminates by ASTM D792-A1. Fiber volume and void volume were calculated from these values, together with weights of graphite and of resin.

Resins EpS-11 and EpIS-1 were chosen for fabrication into 8" x 8" x 0.1" laminates. The choice was based on TGA, isothermal aging, processibility, and the data of Table 20. Prepreg for these laminates was prepared by filament winding, as previously described. Sheets were stacked, placed in a cold press, heated under pressure as shown in Table 21, allowed to cool under pressure, and removed from the press. Two of them were given additional postcure as shown in Table 21. The following laminates were sent to NASA-Lewis for further evaluation: F62-115-1, F62-117-1, F62-118-1, F62-122-2, F62-120-1, F62-122-1, F62-122-3, and F62-123-1.

EXPERIMENTAL

The following preparations are representative of the procedures used. Runs not listed were conducted by similar methods.

Preparation of Polyester Intermediates

F61-126-1. - EG (466 g, 7.5 moles) was stirred while 415 g (2.5 moles) of IP was added. This mixture was cooked at 180°C for 3.5 hrs with nitrogen sparge, using an air condenser. A clear yellow melt was obtained. FU (406 g, 3.5 moles) was then added, together with 2.6 g of a 5% solution of

TABLE 21 - FILAMENT WOUND 8" x 8" GRAPHITE LAMINATES

Resin	I.D.	Laminate No.	Prepreg No.	No. of Plies	Pressure, Psi	Time, Min		Wt. % Resin	Thickness, Mils	% Delamination ^a
						Warmup	Hold at 225°C			
EpS-11E		F62-115-1	F62-114-5 ^b	9	630	100	150 ^d	39	1.23	0
EpS-11E		F62-117-1	F62-114-3 ^c	8	630	120	335	35	100	0
EpS-11E		F62-118-1	F62-114-4	8	630	100	320	38	108	0
EpS-11E		F62-121-2	F62-119-2	8	880	60	420	42	119	61
EpS-11E		F62-122-2	F62-119-1	8	880	60	210 ^e	38	110	5
EpIS-1E		F62-118-2	F62-118-1A	8	630	50	120	30	106	90
EpIS-1E		F62-120-1	F62-119-4	8	940	30	180	36	110	6
EpIS-1E		F62-122-1	F62-118-1A	8	940	120	320	32	93	0.3
EpIS-1E		F62-122-3	F62-119-3	8	940	90	80	38	104	18
EpIS-1E		F62-123-1	F62-118-1	9	630	180	150	32	109	35

^a - Estimated from ultrasonic C scan.^b - Pre cured 2 min at 140-160°C.^c - Pre cured 3 min at 155-170°C.^d - Post cured 280 min at 250°C.^e - Post cured 150 min at 250°C.

hydroquinone in dibutyl phthalate. Cooking was continued for 5 hrs at 180°C and 3 hrs at 200°C to give a clear yellow resin, acid no. 11, 2.7% hydroxyl. Since a higher level of hydroxyl was desired, an additional 150 g of EG was added in portions while the resin was cooked for an additional 12 hrs at 200°C. A clear amber resin was obtained, % hydroxyl: 7.5, 7.8.

F61-151-1. - A mixture of 116 g (1 mole) of FU, 116 g of methyl isobutyl ketone, and 3 g of pyridine was heated to 90°C and stirred at that temperature under reflux while 154 g (2.66 moles) of propylene oxide (PO) was added slowly from a dropping funnel (5 hrs). A clear solution was obtained. Solvent and excess PO were removed by sparging over night with nitrogen at room temperature. The product weighed 230 g (calc. 232 g) and contained 11.0% OH [calc. for bis(hydroxypropyl)fumarate: 14.6%].

Preparation of Polysiloxane Intermediates

D98-65-7. - A solution of 0.6 g (.015 mole) of NaOH in 23.67 g (1.314 moles) of water was added slowly (10 min), with rapid stirring, to 222.4 g (1.5 moles) of DMES. The reaction was slightly exothermic, reaching 32°C. A cloudy yellow solution was produced, which was refluxed for 2 hrs and then cooled to room temperature. Carbon dioxide was bubbled through the product for 30 min. It was then distilled to a pot temperature of 120°C to give 136.5 g of colorless distillate and 106.1 g of residue (98.4% recovery of material). The distillate was mixed with two volumes of water. Two layers formed. The non-aqueous layer was separated and combined with the distillation residue. This solution was dried over

Drierite, filtered, and distilled through a Vigreux column to give 111.8 g of recovered monomer, bp 90-123°C, and 35.43 g of residue, n_D^{20} 1.4035, n_D^{25} 1.4017. The n_D^{20} for $C_2H_5O[Si(CH_3)_2O]_{11}C_2H_5$ is 1.4012³, and n_D^{25} for $[Si(CH_3)_2O]_\infty$ is 1.4035¹², so this material is obviously of high molecular weight. The yield of polymer from unrecovered monomer was about 65%. Toward the end of the distillation, a small amount of cyclic $[(CH_3)_2SiO]_3$ collected in the condenser as a crystalline solid.

D98-69-2. - A solution of 2.00 g (.02 mole) of conc. HCl in 25.77 g (1.5 moles total) of water was added in 90 min to 296.6 g (2 moles) of rapidly stirred DMES. The resulting mixture was refluxed for 30 min and then distilled to a pot temperature of 168°C (vapor temperature 112°C). The distillate weighed 158.5 g (calc., 138.2 g ethanol). It was mixed with twice its volume of water. A small amount of a non-aqueous phase separated, which was added to the distillation residue. The aqueous phase was extracted with hexane, and the extract was also added to the residue, which was then dried over Drierite and distilled to a pot temperature of 216°C (vapor temperature 150°C). Most of this forerun was hexane, with little evidence of DMES. The residue was distilled through a Vigreux column under vacuum to give the fractions shown in Table 22.

F61-115-1. - Absolute ethanol (690 g, 15 moles) was added in 1 hr, with rapid stirring to 645.4 g (5 moles) of dimethyldichlorosilane. A Dry Ice reflux condenser was used, and the exit gas was led to a water trap to absorb HCl. During the addition, the temperature dropped to 11°C and then rose to 36°C. Heat was applied, and the reaction mixture was refluxed for 2 hrs. Titration of the contents of the water trap indicated

TABLE 22 - PRODUCTS FROM PARTIAL HYDROLYSIS OF
DIMETHYLDIETHOXYSILANE WITH DILUTE HCl

Cut No.	Boiling Range, °C/mm Hg	Wt., g	n_D^{20}	<u>n, Average No. of Siloxane Units/Molecule</u>	<u>Yield, %</u>
D98-70-1	38/0.5 - 45/0.15	20.4	1.3923	3	10.4
D98-70-2	45/0.4 - 62/0.10	25.2	1.3940	3.6	13.3
D98-70-3	58/0.2 - 101/0.2	39.1	1.3967	5.0	22.0
D98-70-4	101/0.2 - 102.5/0.2	4.7	1.3981	6.0	2.7
D98-70-5	103/0.2 - 115.5/0.2	4.6	1.3988	6.9	2.7
D98-70-6	116/0.2 - 130/0.2	12.3	1.3990	7.1	7.3
D98-70-7	130/0.2 - 131/0.2	4.5	1.3997	8.1	2.7
D98-70-8	145/0.2 - 177.5/0.2	22.2	1.4005	9.4	13.6
D98-70-9	180/0.2	3.2	1.4013	11	2.0
D98-71-1	Residue	14.0	1.4024	ca. 14	<u>8.8</u>
					85.5 total

that 6.0 moles of HCl had been collected. The product was cooled to room temperature and stirred while 505 g (5 moles) of triethylamine was added over a 1 hr period, followed by 25 g (1.4 moles) of H₂O. The mixture was allowed to stand over night and was filtered to give 617 g (4.5 moles) of solid triethylamine hydrochloride and a clear filtrate. Distillation of the filtrate gave, in addition to a forerun, bp 78-112°C, the fractions shown in Table 23.

F62-15-1. - A solution of 0.5 g NaOH in 15.0 g (0.833 mole) of H₂O was added slowly, with rapid stirring, to 227.9 g (1.25 mole) of MPMS. The mixture was refluxed for 1 hr and then distilled to a pot temperature of 120°C. CO₂ was bubbled through the residual liquid for 2 hrs. This product was filtered to give 161 g (85% yield) of crude trimethyltriphenyl-dimethoxytrisiloxane, n_D^{20} 1.5227.

TABLE 23 - PRODUCTS FROM REACTION OF DIMETHYLDICHLOROSILANE
WITH ETHANOL AND WATER

Cut No.	Boiling Range, °C/mm Hg	Wt., g	n_D^{20}	<u>n, Average No. of Siloxane Units/Molecule^a</u>	<u>Yield, %</u>
F61-116-2	112 - 138/740	22	1.3897	2.3	4.0
F61-116-4	24/1.6 - 63/1.6	47	1.3929	3.3	9.8
F61-116-5	59/1.5 - 69/1.8	16	1.3938	3.5	3.4
F61-116-6	71/1.7 - 93/1.7	27	1.3946	3.8	5.7
F61-116-7	97/2.0 - 107/1.9	25	1.3961	4.6	5.5
F61-116-8	110/1.9 - 138/1.9	39	1.3972	5.4	8.9
F61-116-9	143/1.9 - 175/1.9	35	1.3990	7.1	8.2
F61-116-10	190/3.0 - 206/3.0	17	1.4002	9.0	4.1
F61-116-11	208/2.8 - 232/2.8	15	1.4010	10.5	3.8
F61-116-12	240/2.8 - 244/2.8	8	1.4017	12.0	1.9
F61-116-13	Residue	61	1.4035	ca. 20	<u>15.7</u>
					71 total

a - These values are based upon refractive index. For the lowest boiling fraction, the value is probably somewhat too high because of contamination with triethylamine.

F61-140-1. - A solution of 645 g (5 moles) of DMCS in 600 ml of THF was stirred rapidly while a solution of 45 g (2.5 moles) of water in 300 ml of THF was added over a period of 2 hrs. The solution was refluxed for 2 hrs and distilled to a pot temperature of 135°C to give 369 g (73% yield) of residual colorless liquid, n_D^{20} 1.4104, d_4^{20} 1.0271, which was then distilled through a Vigreux column to give fractions F61-142-1 to F61-142-4 of Table 4.

F61-137-1. - A solution of 573 g (3 moles) of MPSC in 600 ml of THF was stirred rapidly while a solution of 36 g (2 moles) of water in 500 ml of THF was added over a period of 2 hrs. The solution was stirred

for an additional 3 hrs, allowed to stand over night at room temperature, and then distilled to a pot temperature of 230°C to give 494 g (calc. 463 g) of residual liquid, n_D^{20} 1.5317, d_4^{20} 1.1329. Elemental analysis indicates a chain length of approximately 3.7 silicon atoms.

Anal. Calc. for $C_{25.9}H_{29.6}Si_{3.7}O_{2.7}Cl_2$: C, 55.66; H, 5.34; Si, 18.59; Cl, 12.69. Found: C, 55.77; H, 5.76; Si, 17.83; Cl, 12.89.

Redistillation of this liquid gave fractions F61-142-6 and F61-142-7 of Table 4.

Anal. Calc. for $C_{23.1}H_{26.4}Si_{3.3}O_{2.3}Cl_2$: Cl, 14.06. Found: 14.0 (F61-142-6).

Calc. for $C_{43.4}H_{49.6}Si_{6.2}O_{5.2}Cl_2$: Cl, 7.88. Found: 7.94 (F61-142-7).

The physical properties and analyses agree reasonably well with those of Daudt and Hyde.⁶

D98-83-9. - A mixture of 296 g (1 mole) of octamethylcyclotetrasiloxane, 129 g (1 mole) of DMCS and 0.09 g of $FeCl_3$ was held at 50°C in a sealed tube for 28 hrs. The liquid was decanted from the solid residue to give 425 g (100% yield) of greenish liquid with a calculated average composition of $Cl[Si(CH_3)_2O]_4Si(CH_3)_2Cl$.

F62-21-1. - A solution of 32.6 g (0.3 mole) of TMCS, 57.3 g (0.3 mole) of MPSC, and 100 ml of THF was stirred while a solution of 5.40 g (0.3 mole) of water in 100 ml of THF was added over a 1 hr period. The mixture was refluxed for 1 hr and then distilled to a pot temperature of 100°C. The residual product weighed 63.1 g and contained 2.75% Cl (calc. 73.5 g, 14.5% Cl). This Cl content corresponds to a composition of $TMS-MPS_{8.7}Cl$ or to $MPS_{18.5}Cl_2$. The distillate contained 0.6 mole of Cl, presumably present partly as unreacted TMCS and partly as dissolved HCl.

F62-22-2. - The procedure was repeated except that the distillation was continued to a pot temperature of 156°C to give 58.4 g of residual product containing 5.1% Cl. This analysis corresponds to TMS-MPS_{4.3}-Cl or to MPS_{8.7}Cl₂. The distillate contained 0.7 mole of Cl.

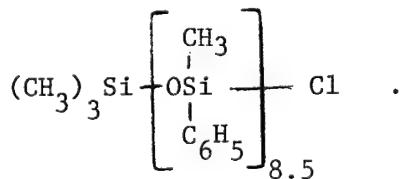
F62-24-1. - The procedure was repeated, using only 2.70 g (0.15 mole) of water. The reflux period was increased to 90 min, and the distillation was taken to a pot temperature of 150°C. The residue weighed 57.9 g and contained 20.4% Cl. This analysis corresponds to a mixture of 2.2 moles of TMS-MPS-Cl and 1 mole of unreacted MPCS or to MPS_{2.2}Cl₂. The distillate contained 0.51 mole of Cl.

F62-27-1. - The procedure was repeated, using 76.8 g (0.4 mole) of MPCS, 21.7 g (0.2 mole) of TMCS, and 7.21 g (0.4 mole) of H₂O. The reflux time was 1 hr and distillation was taken to a pot temperature of 150°C. The residual product weighed 73.6 g and contained 3.0% Cl, which corresponds to TMS-MPS_{7.9}-Cl or to MPS_{16.9}Cl₂.

F62-28-1. - A solution of 32.3 g (0.2 mole) of VCS, 50.8 g (0.47 mole) of TMCS, and 80 ml of THF was stirred rapidly while a solution of 6.6 g (0.37 mole) of water in 13 ml of THF was added over a 1 hr period. The mixture was then refluxed for 1 hr and distilled to a pot temperature of 142°C. The residual product weighed 38.3 g and contained 5.3% Cl (0.06 mole). The HCl that got past the condenser was trapped in water. It amounted to 0.49 mole. The distillate contained 0.40 mole of hydrolyzable Cl and HCl. Total recovery of Cl was 89%.

F62-46-1. - A mixture of 66.7 g (0.56 mole) of TMES, 108 g (0.565 mole) of MPCS, and 0.3 g of FeCl₃ was refluxed for 5 hrs. Effluent

from the reflux condenser was caught in a Dry Ice trap. The trap yielded 51 g of liquid, which was distilled to give 26.9 g of crude ethyl chloride, bp <27°C, and 24.1 g of a mixture of TMCS and TMES, bp 59-90°C. An attempt was made to distil the 103.7 g of residue in the reaction flask under vacuum. A fraction (14 g), bp 66-110°C/740 mm, presumably TMCS + TMES, was recovered from the cold trap, but the remainder failed to distil. It was an oil containing 2.8% Cl, which corresponds to the structure

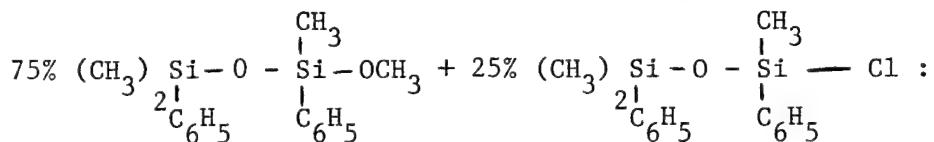


F62-47-1. - A mixture of 91 g (0.5 mole of MPMS, 85.3 g (0.5 mole) of DMPS, and 0.2 g of FeCl_3 was heated gradually to 210°C under reflux. Refluxing occurred during part of the heating period, but stopped toward the end. About 3 g of material passed through the reflux condenser and was collected in a Dry Ice trap. The residue in the flask was distilled at 0.2-0.3 mm to give the following fractions:

	<u>bp, °C at 0.2-0.3 mm</u>	<u>Yield, g</u>
F62-47-2	49 - 50	34.9
F62-47-3	51 - 90	7
F62-47-4	90 - 165	54.2
F62-47-5	165 - 224	38
Residue		10

Elemental analysis of F62-47-2 gave the following results:

C, 62.48; H, 7.62; Si, 17.36; Cl, 2.83; O, 8.47. Calc. for



C, 62.32; H, 7.06; Si, 18.50; Cl, 2.89; O, 9.24.

Preparation of Silicone-Modified Polyesters

D98-75-4 (ES-1). - A mixture of 22.4 g (0.107 mole OH, 0.0574 mole fumarate) of F61-94-2 was warmed with 9.56 g (0.05 mole) of MPCS. HCl was evolved rapidly. The mixture was heated slowly to 200°C and held there for 2 hrs to give a clear amber liquid weighing 28.2 g (calc. 28.3 g), which was cooled to 100°C and dissolved in 6.01 g (0.058 mole) of ST. At room temperature this material was a clear amber solution, viscosity V-W (Gardner). A 5 g sample was mixed with 0.05 g of TBP and heated for 2 hrs at 140°C to give a clear amber resin (D98-77-1). This resin was strong and fairly hard.

D98-77-6 to -9. - The polyester F61-94-2 was heated with the stoichiometric amount of each of the ethoxydimethylsiloxanes D98-74-2, D98-74-5, D98-74-6, and D98-74-7. After 4 hrs at 175-180°C, the mixtures were still incompatible. In the case of D98-74-7, the polyester layer became more viscous, but the others did not change appreciably.

D98-78-1 to -4. - A stoichiometric mixture of F61-94-1 and D98-74-7 was heated with a small amount of each of the following catalysts: tetramethylammonium hydroxide, potassium hydroxide, sodium methoxide, and p-toluenesulfonic acid. During a cook of 1 hr at 150°C and 30 min at 175°C, the first three mixtures became red-brown and apparently reacted slowly as shown by some bubbling, increased viscosity of the polyester layer, and decreased volume of siloxane layer. However they remained incompatible. The last run remained light yellow. It reacted more rapidly than the others, with bubbling and an increase in viscosity of the polyester layer.

The polyester finally became too viscous to stir, while a small amount of siloxane remained as a separate phase. This mixture was not soluble in ST.

D98-79-2 to -7. - Small samples of D98-74-7 were mixed with approximately a 20-fold excess of the polyesters F61-94-2, F61-96-1, F61-94-1, F61-126-1, and F61-131-1. A trace of p-toluenesulfonic acid was added to each mixture, and also to a sample of F61-96-1 by itself. All of them were heated with stirring at 160-180°C. Insoluble gels were formed in all cases. Apparently the catalyst causes gelation of the polyester before the desired condensation reaction occurs.

D98-80-1 (ES-5). - A mixture of 22.1 g (0.1 mole OH, 0.068 mole fumarate) of F61-126-1 polyester and 23.2 g (0.1 g atom Cl) of F61-137-1 (chloro terminated methylphenyltrisiloxane) was heated with stirring. After 3 hrs at 175°C, the solution was heated to 200°C and held at that temperature for 30 min with a slow nitrogen sparge to give 41.8 (calc. 41.6 g) of clear yellow liquid. This product was cooled to 150°C and 7.1 g (0.068 mole) of ST was added. A clear solution was obtained, which became cloudy at room temperature. TBP (0.49 g, 1%) was added, and the resin was cured at 140°C. It became tack free (at 140°C) in less than 45 min, but cure was continued for 18 hrs to give a clear yellow cake (D98-80-5) with a slight oily surface coating. Hardness was Shore D50.

F62-25-2 (ES-37). - A mixture of 20 g of F61-138-1 and 6 g (0.03 g atom Cl) of F62-24-1 was heated for 45 min at 115°C and 1 hr at 125°C to give 24.9 g of product, which was mixed with 7 g of ST. The mixture was not homogeneous. When it was heated in an effort to obtain a homogeneous solution, the product gelled.

F62-13-2 (ES-34). - A mixture of 27.25 g (0.14 mole OH) of F61-138-1 and 14.78 g (0.13 mole) of TMCS was refluxed with stirring for 1 hr. The temperature of the boiling liquid remained at 105-110°C. Material was then distilled to raise the pot temperature. Cooking was continued for 2 hrs at 170°C and 2 hrs at 200°C. The residual product weighed 27.8 g. Apparently there was very little reaction.

F62-17-1. - F61-138-1 (27.25 g, 0.14 mole OH) was melted and stirred at 165°C under reflux while 14.8 g (0.13 mole) of TMCS was added from a dropping funnel during a 3.5 hr period. The mixture was refluxed for an additional 6 hrs at a pot temperature of 130°C. The materials remained incompatible and most of the TMCS was recovered.

F62-19-1 (ES-34). - A solution of 27.25 g (0.14 OH) of F61-138-1 in 50 ml of THF was stirred while a mixture of 11.28 g (0.07 mole) of HMDS and 1 g of TMCS was added. The mixture was refluxed for 30 mins and filtered. The filtrate was boiled down and heated to 180°C to give 31.0 g (calc. 37.3 g) of brown resin, which was dissolved in 10 g of ST. A sample of the solution was catalyzed with 1% TBP and cured at 140°C for 16 hrs to give a resin, Shore D80.

F62-19-2 (ES-34). - A solution of 27.25 g of F61-138-1 in 50 ml of pyridine was stirred while 11.28 g of HMDS was added, followed by 1 g of TMCS. After 10 min at 50°C the mixture was filtered, and the filtrate boiled down to 200°C to give 37.5 g of clear brown residue, which was dissolved in 7.5 g of ST. A sample was catalyzed with 1% TBP and cured at 140°C for 16 hrs to give a clear brown resin, Shore D75.

F62-20-2 (ES-34). - A solution of 27.25 g of F61-138-1 in 40 ml of pyridine was stirred while 11.28 g of HMDS was added, followed by 3 drops

of TMCS. The mixture was allowed to stand over night at room temperature and was then boiled down to 115°C to give 32.2 g of residue, which was dissolved in 7.5 g of ST, catalyzed with 1% TBP, and cured for 16 hrs at 140°C. Shore D hardness was 83.

F62-31-2 (ES-39). - A mixture of 14.5 g (0.053 g atom Cl) of F62-31-1 and 27.1 g (0.053 mole OH) of F61-131-1 was heated slowly to 170°C. The product was cooled to 100°C and dissolved in 9.4 g of ST. A sample was catalyzed with 1% TBP and cured for 16 hrs at 140°C to give a homogeneous resin, Shore D88. The uncured material separated into two layers on standing over night at room temperature.

F62-18-2 (ES-35). - A mixture of 12.5 g (0.065 mole OH) of F62-12-1 and 14.8 g (0.065 mole methoxy) of F62-15-1 was heated for 1 hr at 100-125°C to give 20.1 g (calc. 25.2 g) of product, which was dissolved in 7.5 g of ST. The solution was catalyzed with 1% TBP and cured for 16 hrs at 140°C to give a resin with a Shore D hardness of 84.

D98-98-6 (ES-48). - A mixture of 9.4 g (0.02 mole methacrylate) of D98-97-4 (Table 8) and 6.0 g (0.02 mole fumarate) of F61-131-1 polyester was warmed until the polyester was melted. The two materials were not compatible, so ST was added in 0.02 mole increments as a reactive cosolvent. Addition of 12.5 g (0.12 mole) of ST gave a system that was mostly one phase, with only a trace of a second liquid phase. The mixture was catalyzed with 1% TBP and cured at 140°C for 24 hrs. The product was a clear resin, which appeared homogeneous. However, closer examination revealed that it consisted of two layers, about equal in thickness, which could be split apart. Shore D hardness was 88 for the top layer, 90 for the bottom layer. A second run (D98-97-6) was made in the same way, using the same amounts of

D98-97-4 and ST, with 6.50 g (0.02 mole fumarate) of F61-126-1. Again the cured resin formed two equal layers, top layer Shore D85, and bottom layer Shore D90. A third run (D98-97-8) was made, in which 2-ethoxyethanol was used as a non-reactive solvent. A mixture was made containing 1.625 g of F61-126-1, 2.345 g of D98-97-4, and 4 g of 2-ethoxyethanol. This 50% solution was nearly clear. It was catalyzed with TBP (1% of solids) and baked at 140°C for 24 hrs to give a hazy, fragmented resin, Shore D88.

Preparation of Silicone-Modified Polymethacrylates

The following monomers were used in preparing the methacrylate siloxanes: MAPS, MPMS, and DMES). The procedure used was to mix the silane monomers, add the required amount of water, with a drop or two of conc. HCl, stir for 30 min at room temperature and 30 min at 100°C, and finally sparge with nitrogen for 10 min at 100°C. The products were colorless liquids, samples of which were catalyzed with 1% tert butyl perbenzoate and cured for 16 hrs at 140°C. The compositions prepared are shown in Table 8.

Preparation of Silicone-Modified Epoxies

D98-90-1 (EpS-8). - A mixture of 11.07 g (0.05 mole) of APS, 18.23 g (0.10 mole) of MPMS, and 3.15 g (0.175 mole) of water was stirred. There was a slight exotherm, and a clear, colorless liquid was obtained in about 10 min. After 16 hrs at room temperature it was mixed with 18.8 g (0.1 mole epoxide) of E8 to give a homogeneous liquid. A small sample of this product, heated to 50°C, gelled in 15-20 min. Another sample,

stored at room temperature, gelled in about 90 min. A third sample was cured as shown in Table 11 to give a resin containing 11.1% Si (calc.).

D98-87-4 (EpS-9). - Two siloxanes were prepared. The first was identical to the siloxane portion of D98-90-1. The second was prepared by the same procedure, using 23.63 g (0.1 mole) of GPS, 36.46 g (0.2 mole) of MPMS, and 6.31 g (0.35 mole) of water. The mixture became homogeneous in about 50 min. The two siloxanes were blended to give a clear, colorless liquid of low viscosity. Gel time for this material at room temperature was between 4 and 20 hrs.

D98-93-1. - A mixture of 47.26 g (0.2 mole) of GPS, 72.92 g (0.4 mole) of MPMS, and 12.62 g (0.7 mole) of water was stirred for 1 hr at room temperature to give a colorless solution. This product was heated for 2.75 hrs at 80-90°C, with nitrogen sparging to give 98.50 g of colorless solution. Since hydrolysis appeared incomplete, an additional 12.62 g of water and 2 drops of conc. HCl were added. The solution was stirred for 1 hr at 60°C. It was then sparged with nitrogen at 75-85°C for 1.5 hrs to give a colorless, viscous liquid weighing 88.00 g (calc. 87.94 g for complete conversion of alkoxysilanes to siloxanes). After 6 weeks at room temperature, the material was still a clear, colorless liquid.

D98-94-1 (EpS-10). - A mixture of 4.4 g (0.01 mole epoxy) of D98-93-1 and 0.65 g (0.006 mole anhydride) of PMDA was warmed with stirring. The PMDA gradually dissolved to give at 120°C, a clear yellow solution, which increased in viscosity and formed a soft gum soon after becoming clear. The gum was largely soluble in THF. It was baked for 2.5 hrs at 120°C and 3 hrs at 200°C to give a clear yellow resin, Shore D80.

D98-94-2 (EpS-11). - A solution of 4.4 g of D98-93-1, 0.93 g (.0085 mole anhydride) PMDA, and 25 ml of THF was refluxed for 9 hrs to give a colorless solution of low viscosity, which was boiled down to 7.28 g (73% solids) to give a cloudy, moderately viscous solution. After standing at room temperature over night, the solution deposited a white precipitate. When it was heated further, the precipitate dissolved and the solution gelled at about the same time.

D98-95-2 (EpS-12). - A mixture of 4.4 g of D98-93-1 and 1.37 g (0.0085 mole anhydride) of BTDA was warmed with stirring. It became more viscous and finally gelled before becoming clear. The opaque gel was baked for 3.5 hrs at 140°C and 2 hrs at 200°C to give a tough, opaque resin, Shore D80.

D98-95-3 (EpS-13). - A mixture of 4.4 g of D98-93-1 and 1.09 g (0.00567 mole) of TMA was warmed with stirring until a viscous, nearly clear solution was obtained. It was cured at 140°C for 3.5 hrs and at 200°C for 2 hrs to give a clear yellow resin, Shore D80.

D98-95-4. - The first step in the procedure of D98-90-1 was repeated to give a polysiloxane containing 0.05 mole of amine. The resulting liquid was added in 10 min to a warm solution of 10.91 g (0.05 mole) of PMDA in 125 ml of THF, and the mixture was boiled down to 67.00 g to give a colorless solution of low viscosity, 43.5% solids (calc.). After 5 weeks at room temperature, the product remained a clear colorless liquid.

D98-96-1 (EpIS-1). - A mixture of 11.39 g (0.0085 mole anhydride) of D98-95-4 and 1.88 g (0.01 mole epoxide) of E8 was boiled down to a

weight of 10.0 g (67% solids) to give a clear, viscous solution. It was baked for 2 hrs at 140°C and 2 hrs at 200°C to give a clear yellow resin, Shore D85.

D98-96-2 (EpIS-2). - A mixture of 11.39 g of D98-95-4 and 4.40 g of D98-93-1 was boiled down to 12.0 g (77% solids) to give a colorless, viscous solution, which was baked for 2 hrs at 140°C and 2 hrs at 200°C to give a clear yellow resin, Shore D75.

F32-67-1 (EpIS-1). - The composition of D98-96-1 was prepared on a larger scale, using a small amount of DMF to cut down the amount of THF used. A solution was prepared from 54.5 g (0.25 mole) of PMDA, 313 ml THF, and 23 ml DMF by heating to 50°C. A second solution was prepared by mixing 55.35 g (0.25 mole) of APS, 91.15 g (0.50 mole) of MPMS, and 16 g of H₂O for several minutes. The second solution was added to the first over a 15 min period, keeping the temperature at 40-50°C by intermittent cooling. This solution was then concentrated to 297 g, mixed with 55 g (0.293 eq) of E8, and combined with an equal portion of resin prepared in a like manner. The addition of 50 g of EEA gave a resin of Gardner viscosity B and 56.6% resin solids. This solution was coated on Hercules AS-4 graphite fiber using the filament winding machine to give the prepreg used for laminates F62-70-1, F62-71-3, and F62-80-1 (Table 20).

F32-73-1 (EpS-12). - A mixture of 712 g (3 moles) of GPS and 1,094 g (6 moles) of MPMS was stirred while adding a solution of 30 drops of conc. HCl in 668 g (37 moles) of H₂O. The product was stirred for 2 hrs at 80°C to give a clear solution, which was sparged with N₂ at about 80°C until a weight of 1,386 g was attained. A 353 g (0.764 mole of epoxy)

portion of this material was warmed and stirred while adding a slurry prepared from 104.3 g (0.324 mole) of BTDA, 127 g DMF, 127 g THF, and 25 g DME (warmed to 100°C). The solution was cooled and concentrated to 718 g with nitrogen sparging. Viscosity was Gardner B-C at 64% solids. This solution was coated on Hercules AS-4 graphite fiber on the filament winding machine to give the prepreg used in making laminates F62-86-1, F62-88-1, F62-89-1, and F62-89-2 (Table 20).

F32-91-1 (EpS-11E). - A mixture of 347 g (1.5 moles) of GPS and 592 g (3.0 moles) of MPMS was stirred while adding a solution of 5 drops of conc. HCl in 94.5 g (5.25 moles) of H₂O. After 10 min 132 g (0.6375 mole) of PMDA was added, followed by 200 ml of MOE. The solution was held at 80-100°C for 4 hrs and allowed to cool. EEA and THF were added in portions until a total of 110 ml of each had been added and the viscosity had been reduced to Gardner B. The resulting solution (66% solids) was used in making laminates F62-102-2, F62-103-1, F62-103-2, F62-103-4, and F62-104-1.

F32-92-1 (EpIS-1E). - A mixture of 110.7 g (0.5 mole) of APS, 180.2 g (1.0 mole) of MPMS, and 31.5 g (1.75 moles) of H₂O was stirred until clear (about 10 min). This solution was added with stirring to a solution of 109.1 g (0.5 mole) of PMDA in 1,000 ml of THF. The mixture was refluxed for 30 min, mixed with 1,000 ml of MOE, and refluxed 1 hr. This solution was distilled to a pot temperature of 120°C, cooled to 50°C, and mixed with 110.7 g of E8. The product (Gardner D viscosity) was used for laminates F62-106-2 and F62-106-4.

Preparation of Silicone-Modified Polyimides

F31-77-2. - A nitrating solution was prepared from 58 ml acetic anhydride and 42 ml of 90% fuming nitric acid at about -10°C. To this solution with stirring was added (40 min) 50 g (0.175 mole) of diphenyltetramethyldisiloxane in 250 ml of methylene chloride. The temperature was kept at -7°C or below during addition, and at 10°C or below for the following hour. The resulting material was poured into water and the methylene chloride solution washed with water until the washings were essentially neutral. The solution was dried over night over calcium chloride.

The calcium chloride was removed by filtration and the methylene chloride by evaporation under a stream of nitrogen, leaving about 50 g of a dark oil smelling strongly of nitrobenzene. This material was subjected to vacuum at 5 mm and 100°C but still retained a strong nitrobenzene odor.

The oil was taken up in 200 ml of absolute alcohol and hydrogenated in the presence of 0.5 g 5% pd-on-C at 20-55 psi and a temperature up to 44°C in a small Parr hydrogenator. Total pressure drop was about 64 psi, roughly equivalent to 1 mole, about what would be needed to hydrogenate 0.175 mole containing 2 nitro groups. The mixture was filtered, concentrated under nitrogen, treated with water, extracted with methylene chloride, and dried over sodium sulfate.

The residue after solvent removal was distilled under vacuum to give the following fractions:

90-110°C/0.4-0.5 mm	13.8 g
110-170°C/0.4-0.5 mm, n_D^{20} 1.5476 (lit. 1.5678) ⁹	14.9 g (F31-77-2)
residue	11.2 g

E31-80-1¹⁰. - In a 1 l flask, 50 g (0.207 mole) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added in portions with cooling to 240 ml acetic anhydride. To this solution was added 50 g (0.175 mole) of diphenyltetramethyldisiloxane over about a 30 min period. The temperature was kept at 25-32°C during addition and then kept at 32-38°C for 5 hrs. The solution was cooled and treated with a solution of 200 g of NaOH in 400 g H_2O , keeping the temperature below 40°C. The mixture was extracted twice with methylene chloride and the combined extract was dried over CaCl_2 . The solution was filtered and solvent removed under nitrogen with warming. The remaining oil was hydrogenated as above, giving after solvent removal about 48 g of product. This material was distilled, giving 15 g up to 160°C (0.5 mm), a small dark fraction, 160-170°C, and a dark residue.

A nitrating mixture was prepared by adding 150 ml of acetic anhydride to a solution of 63 g (0.261 mole) $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 100 ml sulfolane with cooling. To this solution was added 50 g (0.175 mole) of diphenyltetramethyldisiloxane in 26 ml of sulfolane. Addition time was 38 min, with the temperature kept below 42°C. The solution was stirred another 25 min and then neutralized with 120 g NaOH in 240 g H_2O . This gave a gooey green mess which was extracted four times with 100 ml portions of methylene chloride. More water was added to the aqueous portion and this mixture was extracted an additional three times with 100 ml portions of methylene chloride. The combined extracts were washed several times with water and dried over CaCl_2 . The dried filtered solution was distilled up to 160°C at 2 mm to remove sulfolane as well as methylene chloride, leaving only 30 g of oily residue. This product was hydrogenated as

before with only about 0.5 mole hydrogen uptake, corresponding roughly to the 30 g yield.

F32-9-1. - To 2 g of the dark hydrogenated oil, 9 g of dimethylacetamide and 1.36 g of PMDA was added. This solution became slightly warm but not notably viscous. A sample was baked out on an aluminum dish to give a brittle film. The remainder of the oil was subjected to distillation in a molecular still. About 10 g was collected that distilled around 170°C at about 0.10 to .15 mm, n_D^{20} 1.5494.

D98-107. - A solution of the diethyl ester of BTDA was prepared by refluxing a mixture of 32.22 g (0.1 mole) of BTDA and 100 ml of anhydrous ethanol for 2 hrs. The resulting clear solution was diluted to 250 ml with anhydrous ethanol to give D98-104-3. A solution of the monoethyl ester of NBA was prepared by refluxing a mixture of 32.83 g (0.2 mole) of NBA and 100 ml of anhydrous ethanol for 2 hrs. A clear solution was obtained. However, when it was diluted to 150 ml with additional ethanol, crystallization occurred. The mixture was further diluted with THF to a volume of 250 ml to give a clear solution, D98-105-1. A mixture of 55.34 g (0.25 mole) of APS, 91.15 g (0.50 mole) of MPMS, and 15.75 g (0.875 mole) of H_2O was stirred until homogeneous (about 10 mins) and then allowed to stand at room temperature for 1 hr to give D98-105-2. The three solutions were blended in various proportions to give the compositions shown in Table 15.

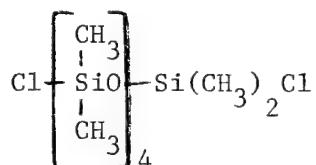
Solid resin samples were prepared by curing a 20.00 g sample of each of the five solutions by the following procedure. Each sample, in an aluminum dish, was heated for 3 hrs in a slow stream of air on a hot plate having a surface temperature of 100°C. Clear, viscous solutions were

obtained. Surface skins formed but were dissolved by stirring. The samples were then heated for 6 hrs at 110°C in a forced draft oven to give clear amber, tough resins containing many large bubbles. They were cured further for 18 hrs at 200°C. There was no change in appearance. Hardness values were difficult to measure because of the bubbles, but all samples were in the range of 80-85 Shore D. All of the samples were strong and tough, with IS-1 judged to be somewhat stronger than the rest. The final weights of the specimens were as follows:

<u>Composition</u>	<u>Wt., g</u>	<u>% of Calc. Wt. for Complete Condensation</u>
IS-1	5.98	98
IS-2	5.98	98
IS-3	6.00	99
IS-4	6.01	99
IS-5	5.85	96

Preparation of Silicone-Modified Phenolics

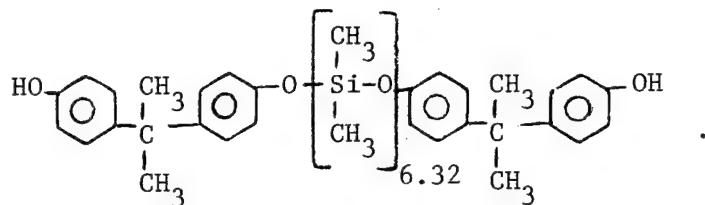
D98-100-3. - A mixture of 45.66 g (0.2 mole) of BPA and 250 ml of 1,1,2-trichloroethane was stirred while 6.8 g (0.4 mole) of anhydrous ammonia was bubbled in over a 30 min period. There was a slight exotherm (38°C), and a clear yellow solution was obtained. This solution was stirred while adding a solution of 40.53 g (0.0952 mole) of



(D98-83-9) in 75 ml of trichloroethane over a 15 min period. A heavy white precipitate formed and the temperature rose to 50°C. The mixture

was stirred for 2 hrs at room temperature and then for 2 hrs at reflux. After cooling, 150 ml of water was added, followed by conc. HCl until strongly acidic. Filtration gave a solid, which was washed with water and with trichloroethane and was dried at 70°C in vacuum to give 7.35 g of tan crystals (D98-100-1). The combined filtrate and washings separated into two layers. The aqueous layer was discarded. The non-aqueous layer was washed five times with water and dried over Drierite. The dry solution was evaporated in a stream of nitrogen to 83 g. A precipitate formed, which was filtered off, washed and dried as before, to give 7.27 g of white powder (D98-100-2). The combined filtrate was evaporated further for 2 hrs at 100°C with nitrogen sparging to give 58.83 g of viscous, amber liquid (D98-100-3).

Analyses of the three products are given in Table 24, together with calculated analyses for BPA and for the composition



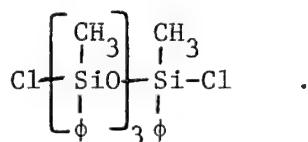
Apparently, D98-100-1 is mostly BPA, D98-100-3 is fairly close to the formula shown, and D98-100-2 is a mixture.

D98-100-4. - A second silicone modified phenolic intermediate was prepared from BPA and MPCS. A solution of 76.45 g (0.4 mole) of MPCS in 150 ml of dry THF was stirred rapidly while adding (1 hr) a solution of 5.40 g (0.3 mole) of H₂O in 100 ml of THF. The resulting solution

TABLE 24 - ANALYSES OF REACTION PRODUCTS OF BPA AND D98-83-9

	Analysis, %				
	C	H	Si	O	Cl
D98-100-1	78.91	7.04	0.44	13.09	0.29
D98-100-2	73.60	7.36	4.76	13.72	0.29
D98-100-3	54.77	7.87	19.56	15.84	0.28
BPA, calc.	78.92	7.06	0	14.02	0
$C_{42.64} H_{67.92} Si_{6.32} O_{9.32}$, calc.	56.45	7.55	19.56	16.44	0

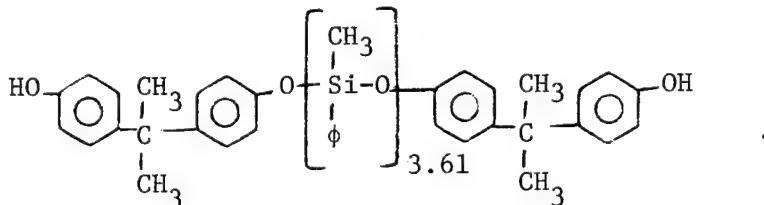
was allowed to stand for 3 hrs and was then boiled down in a stream of dry nitrogen to a weight of 110 g. The product was a colorless solution of siloxane oligomer having an average composition of



D98-100-6. - A solution of 45.66 g (0.2 mole) of BPA in 200 ml of THF was stirred while bubbling in (1 hr) 6.8 g (0.4 mole) of anhydrous ammonia. The resulting clear solution was stirred while adding (5 min) D98-100-4. A heavy white precipitate formed, and the temperature reached 50°C. The mixture was refluxed for 2 hrs, cooled and filtered. The solids were washed with a little THF and then stirred with water. An oil separated, which was extracted from the aqueous phase with chloroform. The chloroform solution was combined with the filtrate. This solution was evaporated in a nitrogen stream and then at 100°C with nitrogen sparging for 3 hrs to give 100.35 g (calc. 98.35 g) of a very viscous tan paste containing some

suspended solid. Anal. Calc. for $C_{55.27}H_{58.88}Si_{3.61}O_{6.61}$: C, 71.35; H, 6.38; Si, 10.90; O, 11.37. Found: C, 69.25; H, 6.28; Si, 10.90; O, 12.53; Cl, 0.87.

This analysis corresponds approximately to the structure



D98-101-1. - An attempt was made to prepare a phenolic resin of the resole type from D98-100-6, using relatively anhydrous conditions to minimize hydrolysis of the phenoxy-silicon linkages. A mixture of 25.09 g (0.025 mole) of D98-100-6, 100 ml of THF, 1.65 g of paraformaldehyde (0.05 mole CH_2O , assuming 9% water), and 1.05 g (0.0025 mole) of 40% benzyltrimethylammonium hydroxide (Triton B) in methanol was refluxed with stirring for 3 hrs. A considerable amount of white solid sublimed onto the upper part of the flask. The reaction mixture was a clear yellow solution containing a small amount of granular solid. A small sample of the solution was baked out on a hot plate to give an oil. Another small sample was acidified with conc. HCl and then baked out to give an oil. Since the reaction appeared incomplete, 100 ml of DMF was added, and the mixture was distilled to a pot temperature of 125°C. An additional 1.65 g of paraformaldehyde and 1.05 g of 40% Triton B were added, and the mixture was stirred at 125-130°C for 1 hr to give a clear yellow solution (D98-101-2) weighing 125 g. A 1.00 g sample of D98-101-2 was baked for 16 hrs at 120°C to give a liquid product. Further baking for 6 hrs at

175°C gave two liquid phases. The procedure was repeated, using 1.00 g of D98-101-2 and 1 drop of conc. HCl, and again using 1.00 g of D98-101-2 and 4 drops of TMCS. Both samples gave products consisting of two liquid phases.

CONCLUDING REMARKS

Most of the silicone-modified unsaturated polyesters that were prepared were not homogeneous. The highest silicon content among the homogeneous resins of this class corresponds to a silica residue of 21%. The actual residues found after heating these resins to 1,000°C in air or nitrogen were, in most cases, less than the calculated values. The loss of silicon is believed to be due to the formation of volatile cyclic siloxanes or silicate esters upon heating. Because of these limitations this class of resins was not evaluated in graphite laminates.

Silicone-modified thermosetting methacrylates were prepared with calculated silica residues up to 63%, but better physical properties were found in a composition predicted to yield 40% silica. The actual char yield at 1,000°C was 32%. In isothermal weight loss determinations in air at 175-225°C, this resin had one of the lowest rates of weight loss of the polymers tested. Because of time limitations and difficulties in preparing suitable B-stage prepreg, the methacrylates were not evaluated extensively in laminates. Further study of prepegging conditions for this class of resins appears justified.

Silicone-modified epoxies of both amine cured and anhydride cured types were prepared. In general, the amine cured systems set up too

rapidly for convenience in a B-stage prepreg system. Excellent results were obtained with anhydride cured systems of several types. In one system, epoxy groups were furnished by a commercial epoxy resin of the bisphenol type, with a curing agent containing siloxane, imide, and anhydride groups. Another system employed the same curing agent with a glycidoxypipropyl siloxane as the source of epoxy groups. A third system combined a glycidoxypipropyl siloxane with an anhydride, such as PMDA or BTDA. Four resins of these types were selected for evaluation. Calculated silica yields were 22.5-35.7%. The actual char yields at 1,000°C were 20.1-39.6%, and averaged 1.2 times the calculated values.

Graphite fiber prepgs, prepared from the four epoxy silicones by filament winding, were fabricated into unidirectional laminates. Although prepreg and pressing conditions were not fully optimized, well consolidated laminates were obtained. For the better laminates, flexural strengths exceeded 100 kpsi, flexural modulus exceeded 10 Mpsi, and interlaminar shear strengths were about 5 kpsi. Four 8" x 8" x 0.1" laminates from each of two of the resins were sent to NASA-Lewis for further evalaution. The anhydride cured epoxy silicones have demonstrated good processing and performance characteristics. Further investigation of resin formulation and fabrication conditions can be expected to give improved processibility and physical properties.

One of the aminopropyl siloxanes prepared as an intermediate for epoxy silicones was also used as a polyamine in the preparation of silicone-modified polyimides of the PMR type. Calculated silica residue for these resins was 34%, and the average observed char weight at 1,000°C

was 43%. Time did not permit evaluation in laminates, but the cured polymers were hard and appeared to have suitable processing characteristics. Further research is needed for an adequate evaluation.

Two classes of silicone-modified phenolic resins were prepared by curing phenolic substituted siloxanes with hexamethylenetetramine. Calculated silica residues for one class were about 46% and average char yields at 1,000°C were about 39%. For the second class, calculated silica was about 23% and char yield about 41%. No laminates were made from these resins but they have good cure characteristics and hardness. Additional work is needed to determine their usefulness.

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1. Report No. NASA CR-159750	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle SILICONE MODIFIED RESINS FOR GRAPHITE FIBER LAMINATES		5. Report Date September 28, 1979	
		6. Performing Organization Code	
7. Author(s) L. W. Frost and G. M. Bower		8. Performing Organization Report No. 79-9B7-SICOP-R1	
9. Performing Organization Name and Address Westinghouse R&D Center 1310 Beulah Road Pittsburgh, PA 15235		10. Work Unit No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		11. Contract or Grant No. NAS3-21373	
		13. Type of Report and Period Covered Contractor Report	
		14. Sponsoring Agency Code	
15. Supplementary Notes Project Manager, R. W. Lauver, Materials and Structures Division NASA Lewis Research Center, Cleveland, Ohio			
16. Abstract When graphite fiber composites are burned, the liberated fibers may settle on electrical apparatus and cause severe damage. This problem can be minimized by bonding the fibers with silicone modified laminating resins that leave a siliceous residual char when they are burned. During the first year of this program, 85 silicone modified resins have been synthesized and evaluated for this application. Included were unsaturated polyesters, thermosetting methacrylates, epoxies, polyimides, and phenolics. Neat resins were judged in terms of Si content, homogeneity, hardness, char formation, and thermal stability. Char formation was estimated by thermogravimetry to 1,000°C in air and in N ₂ . Thermal stability was evaluated by isothermal weight loss measurements for 200 hrs in air at three temperatures. Four silicone modified epoxies were selected for evaluation in unidirectional filament wound graphite laminates. Neat samples of these resins had 1,000°C char residues of 25-50%. The highest flexural values measured for the laminates were a strength of 140 kpsi and a modulus of 10 Mpsi. The highest interlaminar shear strength was 5.3 kpsi. Two of the resins were used to make 8" x 8" x 0.1" flat unidirectional laminates, which have been shipped to NASA-Lewis for further evaluation.			
17. Key Words (Suggested by Author(s)) laminates, graphite, silicone, phenolics, epoxy, polyester, polyacrylates, polyimides, char, filaments, winding, thermal, stability		18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 77	22. Price*

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